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Page. Line
i, 216 bottom for "m.p. 240°" read "m.p. 204°."

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i, 780 17
19
20
10*
9*
4* } for "Nitrous oxide" read "Nitric oxide."
ii, 1210, col. i. 32
36
ii, 1337 ,, 28
ii, 1390, col. ii. 19*

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i, 326 18
21 } for "Nitrous oxide" read "Nitric oxide."
ii, 934, col. ii. 16
ii, 1079 ,, 8-10 the entry "behaviour of various substances with
(FANZER) A., i, 326," should be transposed to
line 19 (under nitrogen dioxide).

* From bottom.

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* From bottom.

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XXXIV.—*Porphyroxine.*

By JITENDRA NATH RAKSHIT.

THE ethereal extract obtained in the estimation of morphine in opium by the process described by the author (*Analyst*, 1918, **42**, 320) left a viscid, brown, crystalline residue on evaporation, which when dissolved in dilute acid always gave a solution, becoming more and more purple on stirring or heating. Previous authors do not agree regarding the composition of this colouring matter; Merck, in 1837, prepared from opium a substance containing its colouring matter, and called it porphyroxine; Hesse remarked (*Annalen*, 1870, **153**, 47) that the substance prepared by the former investigator was a mixture of several alkaloids, one of which is meconidine and another probably rhœadine. The same author (*Annalen, Suppl.*, 1864—1865, **4**, 50) noted that Merck's porphyroxine agrees with rhœadine in method of preparation, properties, and composition. It was thought desirable to investigate whether here is any alkaloid that may be correctly called porphyroxine in Indian opium. The alkaloid now isolated was very likely a constituent of what Dey (*Pharm. J.*, 1882, [iii], **12**, 397) obtained on vaporation of the ethereal extract prepared by shaking an aqueous solution of opium made alkaline with sodium carbonate or ammonia, and apparently also of what Merck called porphyroxine. Considering these facts and that the alkaloid gives a purple solution with dilute acids resembling porphyrin, the name porphyroxine may reasonably be retained.

The alkaloid isolated is fairly readily soluble in water, in which aspect only it resembles papaverine, codamine, narceine, and codeine, but its other properties are in striking contrast with them; the solutions of the base or its salts are strongly levorotatory, it does not sublime like codamine, and, unlike codeine, the aqueous solution of its hydrochloride gives a white or pale yellow precipitate with ammonia.

Preparation.—Twenty parts of Indian opium powder and nine parts of freshly slaked lime were triturated in a mortar for five minutes, then 100 parts of water were added gradually during one hour, the trituration being continued. The solution was filtered and the filtrate shaken with an equal bulk of ether for ten minutes in a separator. The ethereal layer was then filtered into another separator containing some dry lumps of calcium chloride, shaken for five minutes, allowed to settle, the ethereal solution decanted, filtered, and evaporated on a water-bath. A pale yellowish-brown,

soft, crystalline residue was obtained, which when rubbed with a spatula on a porcelain plate for three to four hours became a dry powder. One hundred grams of this powder were heated with 200 c.c. of light petroleum until the solvent boiled briskly, the whole was shaken for fifteen minutes, heated again to boiling, and the petroleum decanted as completely as possible, the insoluble residue being carefully excluded. This process of extraction was repeated five times, 100 c.c. of petroleum being used each time, and finally the contents of the flask were collected, dried, and powdered. Ten grams of this powder were triturated with 100 c.c. of 10 per cent. hydrochloric acid gradually added during half an hour, and then with 100 c.c. of water gradually added during another hour, and filtered quickly, the residue being washed with a little dilute hydrochloric acid. To the filtrate was added a saturated solution of sodium hydrogen carbonate, a thin layer of ether being kept on the surface of the liquid, and the latter was stirred until the addition of a further quantity did not produce any effervescence. After remaining for half an hour for the complete separation of the precipitate, this was collected and washed with distilled water. The filtrate, measuring about 500 c.c., was shaken with 50 c.c. of chloroform for fifteen minutes, the chloroform removed, and the process of extraction was similarly repeated thrice with 30, 25, and 25 c.c. of chloroform respectively. The chloroform extracts were mixed together, filtered, the bulk of the solvent was distilled off, and the residue dried slowly on the water-bath; it was then kept overnight in a desiccator. Sometimes the substance formed a soft, viscid, crystalline mass, but generally a pale brownish-yellow, viscid varnish, which on rubbing with a spatula against the side of the basin for an hour became a crystalline, pink powder. Five grams of this powder were heated on a water-bath with 100 c.c. of light petroleum (b. p. 100–120°) just to boiling, the mixture was then shaken for fifteen minutes with a rotatory motion, heated again to boiling, and the petroleum decanted through filter paper, the undissolved residue being carefully excluded. The residue in the flask was again twice extracted similarly with 80 and 60 c.c., respectively, of light petroleum, care being always taken not to melt the substance, thus causing the extraction to be incomplete. The successive petroleum extracts were collected and allowed to evaporate, when the base crystallised in groups of radiating shining, pale yellow prisms, which were carefully separated from a thin film of non-crystalline residue, powdered, and dried in a desiccator. Several samples from different preparations were analysed, the results of one only being given below:

0.2950 gave 0.7530 CO_2 and 0.1854 H_2O . $\text{C}=69.46$; $\text{H}=6.98$.
 0.253 ,, 10.6 c.c. N_2 (moist) at 34° and 750 mm. $\text{N}=4.36$.
 $\text{C}_{19}\text{H}_{23}\text{O}_4\text{N}$ requires $\text{H}=6.99$; $\text{C}=69.30$; $\text{N}=4.26$ per cent.

Porphyroxine forms pale yellow or white, transparent prisms melting at $134\text{--}135^\circ$ to a clear, transparent, straw-coloured liquid which solidifies on cooling. It is a non-deliquescent substance appreciably soluble in water, giving a strongly alkaline solution; it is readily soluble in dilute acids, acetone, carbon disulphide, chloroform, or glacial acetic acid, moderately so in benzene, carbon tetrachloride, methyl or ethyl alcohol, toluene, or ethyl acetate, sparingly so in amyl alcohol, ether, light petroleum, ammonia, or arium hydroxide, and almost insoluble in aqueous sodium hydroxide, potassium hydroxide, or lime water. When its dilute mineral acid solutions are kept exposed to air, they assume a fine pink porphyry colour. The base has a strongly alkaline reaction towards cochineal, methyl-orange, and litmus, but has no action on phenolphthalein. Iodine solution gives an orange precipitate with the aqueous solution of the base and a brick-red precipitate with its dilute hydrochloric acid solution. Mayer's reagent gives a white precipitate with its aqueous solution and the usual pale yellow one with its dilute hydrochloric acid solution. Colour reactions of the base are often vitiated by the presence of a small quantity of impurity, and the following reactions were observed with a sample specially prepared by recrystallising three times from petroleum. It gives a red colour with concentrated sulphuric acid, a grass-green with concentrated sulphuric acid and a small quantity of potassium dichromate, a pale yellow with concentrated nitric acid, and an orange with concentrated hydrochloric acid; a brownish-red precipitate is obtained on adding ferric chloride to its sulphuric acid solution, and when fused with potassium hydroxide it becomes brown and gives off a strongly alkaline vapour without becoming charred.

0.2540, made up to 50 c.c. with chloroform, gave $\alpha - 4.1^\circ$ (Vrentze) in a 2-dm. tube at 32° , whence $[\alpha] - 139.9^\circ$.

The *hydrochloride* crystallises from water in prismatic needles. It is a stable salt, and, on heating, softens at 140° and melts at 155° to a clear, pale yellow liquid which does not solidify quickly on cooling:

0.1168 gave 0.0460 AgCl . $\text{Cl}=9.7$.

$\text{C}_{19}\text{H}_{23}\text{O}_4\text{N.HCl}$ requires $\text{Cl}=9.7$ per cent.

It is a non-deliquescent, crystalline, stable substance readily soluble in water, chloroform, methyl or ethyl alcohol, or glacial acetic acid, sparingly so in amyl alcohol or carbon disulphide, and

almost insoluble in acetone, benzene, carbon tetrachloride, ethyl acetate, ether, light petroleum, or toluene.

0.2920, made up to 50 c.c. with water, gave $\alpha - 4.0^\circ$ (Ventzke) in a 2-dcm. tube at 32° , whence $[\alpha] - 118.8^\circ$.

The *platinichloride* separates from a fairly concentrated aqueous solution as a bright, ochreous, crystalline powder.

Found: Pt=18.0.

$(C_{19}H_{22}O_4N, HCl)_2PtCl_4$ requires Pt=18.2 per cent.

When kept in a steam-oven for a long time, it slowly swells up and decomposes, forming a dark brown, spongy mass. It darkens at 188° and melts and decomposes at about 204° .

The *aurichloride* was obtained as a greyish-yellow, amorphous precipitate, which decomposed within an hour while remaining in the mother liquor.

The *hydrobromide* crystallises in fine, white needles which melt at $148-150^\circ$ to a pink liquid:

0.3367 gave 0.1555 AgBr. Br=19.7.

$C_{19}H_{22}O_4N, HBr$ requires Br=19.5 per cent.

It becomes slightly pink after two or three days, and is readily soluble in water, methyl or ethyl alcohol, or glacial acetic acid, sparingly so in acetone, chloroform, or ethyl acetate, and insoluble in amyl alcohol, benzene, carbon disulphide, carbon tetrachloride, ether, light petroleum, or toluene.

0.4209, made up to 50 c.c. with water, gave $\alpha - 4.4^\circ$ (Ventzke) in a 2-dcm. tube at 32° , whence $[\alpha] - 90.6^\circ$.

The *hydriodide* was obtained as a pale brown powder, which melts and decomposes at 115° . The salt, once separated from its aqueous solution, is very sparingly soluble in water, and therefore in the analysis the silver iodide was precipitated from its alcoholic solution:

0.1560 gave 0.8200 AgI. I=28.3.

$C_{19}H_{22}O_4N, HI$ requires I=27.8 per cent.

It is readily soluble in methyl or ethyl alcohols, very sparingly so in water, acetone, chloroform, ethyl acetate, or glacial acetic acid, and insoluble in amyl alcohol, benzene, carbon disulphide, carbon tetrachloride, ether, light petroleum, or toluene.

0.3120, made up to 50 c.c. with alcohol, gave $\alpha - 2.8^\circ$ (Ventzke) in a 2-dcm. tube at 32° , whence $[\alpha] - 77.8^\circ$.

The *sulphate* separated from water in pale pink, radiating plates which, when washed with a mixture of equal parts of absolute alcohol and ether, melted at 193° to a pink liquid, with slight decomposition:

0.5120 gave 0.1794 BaSO_4 . $S=4.8$.

$(\text{C}_{19}\text{H}_{23}\text{O}_4\text{N})_2 \cdot \text{H}_2\text{SO}_4$ requires $S=4.3$ per cent.

It is readily soluble in carbon tetrachloride, chloroform, ethyl alcohol, or toluene, and almost insoluble in acetone, amyl alcohol, benzene, carbon disulphide, ethyl acetate, ether, or light petroleum.

0.5600, made up to 50 c.c. with water, gave $\alpha-7.2^\circ$ (Ventzke) in a 2-dm. tube at 32° , whence $[\alpha] -111.4^\circ$.

The *phosphate* did not crystallise from water, but was obtained as a powder, which melted at 117° to a pale brown, transparent liquid:

0.4312 gave 0.1175 $\text{Mg}_2\text{F}_6\text{O}_7$. $P=7.6$.

$\text{C}_{19}\text{H}_{23}\text{O}_4\text{N} \cdot \text{H}_3\text{PO}_4$ requires $P=7.3$ per cent.

This salt quickly absorbs moisture when left exposed to a damp atmosphere, and becomes viscous. It is readily soluble in water, alcohol, methyl alcohol, or glacial acetic acid, sparingly so in chloroform, ethyl acetate, or ether, and insoluble in acetone, amyl alcohol, benzene, carbon disulphide, carbon tetrachloride, light petroleum, or toluene.

0.5390, made up to 50 c.c. with water, gave $\alpha-6.1^\circ$ (Ventzke) in a 2-dm. tube at 32° , whence $[\alpha] -98.2^\circ$.

The *nitrate* crystallises from water in voluminous, fine, feathery aplets melting at 122° to a transparent, pink liquid. An attempt was made to determine the nitric nitrogen by the Crum-Frank and method, but as soon as sulphuric acid was mixed with a solution of 0.1367 gram of the nitrate in the nitrometer, a blood-red coloration was at once produced, and only 1.0 c.c. of moist nitric oxide was evolved at 35° and 750 mm. The percentage of nitric nitrogen thus found is only 0.38, whilst that required for $\text{C}_{19}\text{H}_{23}\text{O}_4\text{N} \cdot \text{HNO}_3$ is 3.80 per cent. Moreover, duplicate analyses did not always agree, and the nascent nitric acid reacts with the alkaloid before it does with mercury:

0.1965 gave 0.4240 CO_2 and 0.1090 H_2O . $C=58.7$; $H=6.1$.

$\text{C}_{19}\text{H}_{23}\text{O}_4\text{N} \cdot \text{HNO}_3$ requires $C=58.2$; $H=6.1$ per cent.

It is readily soluble in water, chloroform, methyl or ethyl alcohol, glacial acetic acid, acetone, or carbon disulphide, sparingly in benzene, carbon tetrachloride, ethyl acetate, ether, or toluene, and insoluble in amyl alcohol or light petroleum.

0.6835, made up to 50 c.c. with water, gave $\alpha-9.1^\circ$ (Ventzke) in a 2-dm. tube at 32° , whence $[\alpha] -115.4^\circ$.

The acetate was obtained as a pale brown, transparent, viscid mass:

0.2780 gave 0.6610 CO_2 and 0.1920 H_2O . $\text{C}=64.8$; $\text{H}=7.6$.

$\text{C}_{19}\text{H}_{22}\text{O}_4\text{N}_2\text{C}_2\text{H}_4\text{O}_2$ requires $\text{C}=64.8$; $\text{H}=7.0$ per cent.

It is readily soluble in water, chloroform, methyl or ethyl alcohol, or glacial acetic acid, sparingly so in acetone or ethyl acetate, and insoluble in amyl alcohol, benzene, carbon disulphide, carbon tetrachloride, ether, light petroleum, or toluene.

The *oxalate* crystallises from water in long, pale yellow, prismatic crystals, which darken and melt at 182° with effervescence:

0.1670 gave 0.0492 CaC_2O_4 . $\text{C}_2\text{H}_2\text{O}_4=20.72$.

$\text{C}_{19}\text{H}_{22}\text{O}_4\text{N}_2\text{C}_2\text{H}_2\text{O}_4$ requires $\text{C}_2\text{H}_2\text{O}_4=21.48$ per cent.

It is fairly readily soluble in water, methyl alcohol, or glacial acetic acid, sparingly so in acetone, ether, or ethyl alcohol, and insoluble in amyl alcohol, benzene, carbon disulphide, carbon tetrachloride, chloroform, ethyl acetate, light petroleum, or toluene.

0.9340, made up to 50 c.c. with water, gave $\alpha=12.3^\circ$ (Ventzke) in a 2-dm. tube at 32° , whence $[\alpha]=-114.2^\circ$.

The *citrate* is an amorphous, yellowish-white powder, which melts at $82-85^\circ$ to a transparent, pale brown liquid:

0.1135 gave 0.2680 CO_2 and 0.0735 H_2O . $\text{C}=64.3$; $\text{H}=7.1$.

$(\text{C}_{19}\text{H}_{22}\text{O}_4\text{N}_2)_3\text{C}_6\text{H}_8\text{O}_6$ requires $\text{C}=64.1$; $\text{H}=6.4$ per cent.

It is appreciably hygroscopic, readily soluble in water, methyl or ethyl alcohol, or glacial acetic acid, sparingly so in acetone, amyl alcohol, carbon disulphide, chloroform, or ethyl acetate, and insoluble in benzene, carbon tetrachloride, ether, light petroleum, or toluene.

0.1595, made up to 50 c.c. with water, gave $\alpha=2.0^\circ$ (Ventzke) in a 2-dm. tube at 32° , whence $[\alpha]=-108.6^\circ$.

The *tartrate* is a pink, crystalline powder, which melts at $116-118^\circ$ to a pale brown, transparent liquid:

0.1080 gave 0.2475 CO_2 and 0.0650 H_2O . $\text{C}=62.5$; $\text{H}=6.6$.

$(\text{C}_{19}\text{H}_{22}\text{O}_4\text{N}_2)_2\text{C}_4\text{H}_6\text{O}_6$ requires $\text{C}=62.4$; $\text{H}=6.4$ per cent.

It is somewhat hygroscopic, readily soluble in water, methyl or ethyl alcohol, or glacial acetic acid, sparingly so in amyl alcohol, benzene, carbon disulphide, chloroform, or ethyl acetate, and insoluble in acetone, carbon tetrachloride, ether, light petroleum, or toluene.

0.1635, made up to 50 c.c. with water, gave $\alpha=1.8^\circ$ (Ventzke) in a 2-dm. tube at 32° , whence $[\alpha]=-95.5^\circ$.

The *picrate* is a bright yellow, crystalline powder, which becomes brown at 171° and melts at 198° :

0.1158 gave 0.2258 CO_2 and 0.0510 H_2O . $\text{C}=53.2$; $\text{H}=4.8$.

$\text{C}_{19}\text{H}_{22}\text{O}_4\text{N}_2\text{C}_6\text{H}_3\text{O}_7\text{N}_3$ requires $\text{C}=53.7$; $\text{H}=4.7$ per cent.

It is a non-deliquescent, crystalline powder, readily soluble in acetone, chloroform, methyl or ethyl alcohol, glacial acetic acid, or ethyl acetate, sparingly so in water, amyl alcohol, benzene, or carbon disulphide, and almost insoluble in carbon tetrachloride, ether, light petroleum, or toluene.

0.2658, made up to 50 c.c. with water, gave $\alpha - 1.5^\circ$ (Ventzke) in a 2-dcm. tube at 32° , whence $[\alpha] - 49.9^\circ$.

OPIMUM FACTORY,
GAZIPUR, INDIA.

[Received, October 31st, 1918.]

XXXV.—Coagulation of Metal Sulphide Hydrosols. Part I. Influence of Distance between the Particles of a Sol on its Stability. Anomalous Protective Action of Dissolved Hydrogen Sulphide.

By JĀNANENDRA NATH MUKHERJEE and NAGENDRA NATH SEN.

THE coagulation of the sulphide sols has been studied by a fairly large number of investigators. There is, however, fundamental disagreement between the results obtained by different authors. It was suggested by one of us in a previous paper (*J. Amer. Chem. Soc.*, 1915, **37**, 2024) that the discrepancy is due to the difference in the methods of observation, some of which are undoubtedly defective. The method used in that paper is a comparative one, and is based on visual observation of the changes in the sol with time. It will be conceded that no objection can be taken against it, although it has one disadvantage in so far as it is not instrumental. This does not in any way interfere with the trend of the results. The method is found to be the most suitable one and gives concordant numbers.

Contrary to the observations of Freundlich (*Zeitsch. physikal. Chem.*, 1903, **44**, 129), it was shown that dilution with pure water increases the stability of arsenious sulphide hydrosols to coagulation by electrolytes. The electrolytes studied were all salts of univalent cations. The difficulty in explaining the observed facts on the basis of the adsorption theory as developed by Freundlich (*loc. cit.*; *ibid.*, 1910, **73**, 385; 1913, **83**, 97; **85**, 398, 641) was mentioned. This point has also received attention from Kruyt and Spek. (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **17**, 1158), who examined three electrolytes, namely, the chlorides of potassium,

barium, and aluminium, but could not find the stabilising influence of dilution of the sols for ions other than potassium. They do not seem to recognise that the adsorption theory as it stands is insufficient to explain all the facts observed, and do not consider the influence that the distance between the particles of the sol may have on the stability of the sol.

Further, Young and Neal (*J. Physical Chem.*, 1917, **21**, 14), in a thorough study of cupric sulphide hydrosols, remark: "the amount of electrolyte required is independent of the dilution of the sol within wide limits. This latter was found to be true within rather close limits by Freundlich for arsenic sulphide sols." The method used by Young and Neal consists in mixing equal volumes (2 c.c. each) of electrolyte and sol and noting the respective concentration of electrolyte that just produces complete separation of the colloid in twenty-four hours and that which just fails to do so. These two limiting concentrations give a measure of the stability of the sol or the coagulative power of the electrolyte. This method is one due to Freundlich, and generally used by other workers. It will be noted that the concentrations of electrolytes employed are, necessarily, such as would require a fairly long time for the complete separation of the colloid. In the earlier paper (*loc. cit.*), the process of coagulation was discussed in detail, and it was stated that "the time for complete settling is not characteristic of the rate of coagulation." The justification of any method lies in so far as it indicates the progress of coalescence. The increased mass of particles with progress of coalescence introduces a new factor, namely, their gravitational effect, which masks the true behaviour of the sol, as will be clear from the following observations on mercuric sulphide sols.

These sols are opaque unless very dilute. On the addition of electrolytes, there is a quiescent period followed by a sharp clearing of the whole liquid. At this stage, the liquid loses its homogeneous appearance, and visible clots are found suspended throughout the liquid. As the change is sharp, the times noted by different observers agree satisfactorily. In this way, it is found that a mercuric sulphide sol, on saturation with hydrogen sulphide, requires a longer time for the observed change than when it is not so treated—the electrolyte concentration, of course, being identical.

These experiments leave no doubt that dissolved hydrogen sulphide increases the stability of the sol. The subsequent settling of these clots, however, requires a very long time, which is about the same for both samples. So long as the respective times required for the clearing of the sols are very small compared with the time required for the subsequent settling of the clots, it is found that

the times that are necessary for the complete separation of the colloid do not differ much in the two cases. However, with electrolyte concentrations where the clearing requires intervals comparable with that required for the subsequent settling of the clots, regular differences in stability are observed even if the times necessary for complete separation of the colloid are noted.

Influence of Dilution on the Stability of a Sol.

The method employed is to mix 5 c.c. each of sol and electrolyte in carefully cleansed test-tubes. For reasons discussed in the previous paper, the electrolyte is always added to the sol. Thorough mixing is secured by pouring the mixed liquids from one test-tube to another and repeating the process. The mixed liquid is shaken regularly at short intervals, and the changes with time are observed. As before, the times required for perceptible change in the sol, for the attainment of maximum opacity, and for the first appearance of visible particles are noted. The time for complete separation of the colloid is also noted when thought desirable. The comparison is always carried out side by side. For sols of mercuric and cupric sulphides, the time for the appearance of visible particles is noted. With dilute sols, it is necessary to note the time for complete settling of the particles.

Experiments were made on arsenious sulphide sols with solutions of hydrogen, ammonium, potassium, lithium, barium and aluminium chlorides, aluminium sulphate, and thorium nitrate. With sols of mercuric and cupric sulphides, solutions of potassium, ammonium and barium chlorides, aluminium sulphate, and thorium nitrate only were studied. All the glass vessels were cleansed by tipping them for twenty-four hours in chromic acid solution after they had been washed with dilute alkali hydroxide. The need for scrupulous care in the washing of the vessels and avoiding dust or other impurities cannot be too strongly emphasised. This holds especially for the extremely dilute solutions used in some cases.

(a) Arsenious Sulphide Sols.

In the presence of salts having univalent cations, dilution of the sol increases its stability in each case. The magnitude of the stabilising effect of dilution will be evident from table I. The electrolyte concentrations given are end concentrations, that is, what results after mixing. Sols mentioned in the several tables are different unless stated otherwise. "Coagulation" means the

breaking up of the colloid into flakes so that the liquid is clear or very slightly coloured.

TABLE I.

Sol A contained 17.58 millimoles of arsenious sulphide per litre. Sol B was prepared by diluting sol A five times, and sol C by diluting sol A ten times, with pure water.

Electrolyte: lithium chloride.

| Dilution (after mixing). | Sol. A. | Sol. B. | Sol. C. |
|-----------------------------|--|---|--|
| 5N/16 ... | — | — | Coagulation after 20 seconds. |
| 5N/32 ... | — | Coagulation after 30 seconds. | Coagulation after 50 minutes. |
| N/8..... | Instantaneous coagulation. | Coagulation after half an hour. | Perceptible change after 8 minutes. Coagulation after 2½ hours. |
| N/16 ... | Change perceptible on mixing. Coagulation not observed after 1½ hours. | Change just after mixing not per- ceptible. | Change perceptible after 45 minutes. |

On the other hand, in the presence of the salts of aluminium and thorium, the stability decreases on dilution, as will be seen from table II. The data refer to the same three sols. The observations in tables I and II were completed within two days, and neglecting the slight "ageing" during this interval, the data may be taken as comparable.

TABLE II.

Electrolyte: thorium nitrate.

| Dilution. | Sol. A. | Sol. B. | Sol. C. |
|-----------|---|---|--------------------------------------|
| N/10,000 | Instantaneous coagulation. | Instantaneous coagulation. | Instantaneous coagulation. |
| N/20,000 | Perceptible turbidity just after mixing. Sol changes slowly. | Coagulation in 2 minutes. | Coagulation within half a minute. |
| N/30,000 | Perceptible turbidity after half an hour. | Perceptible turbidity after 5 minutes. | Coagulation in 4 minutes. |
| N/40,000 | — | — | Coagulation in 53 minutes. |

Solutions of salts of bivalent cations display an interesting aspect of the effect of dilution of the sol on its stability. With dilute

sols, the stability increases on dilution, whereas with sols very rich in sulphide content, the stability diminishes on dilution, and for a rich sol it is possible to reach a limit where on further dilution the sol becomes more stable. Moreover, from table III it will be seen that the stability relations on dilution vary with the concentration of the electrolyte itself.

TABLE III.

Electrolyte: barium chloride.

Arsenious sulphide sol containing 19.45 millimoles per litre.

| Dilution of Electrolyte. | Original Sol. | Sol diluted 4 times. | Sol diluted 16 times. |
|-----------------------------|---|---|---|
| N/800 ... | Complete coagulation in 1 minute. | Change perceptible in 26 seconds. Coagulation after 4 minutes. | Perceptible change after 1 minute. Coagulation after 12 minutes. |
| N/1000 ... | Change perceptible after half a minute. Clots appear throughout after 17 minutes. | Change perceptible in 1 minute. Clots appear throughout after 18 minutes. | Change perceptible after 2 minutes. Clots appear throughout after 26 minutes. |
| N/1200 ... | Change perceptible in 2 minutes. Clots appear after 1 hour 7 minutes. | Change perceptible in 2 minutes. Clots appear after 52 minutes. | Change perceptible after about 3 minutes. Clots appear after 1 hour 1 minute. |

(b) *Mercuric and Cupric Sulphide Sols.*

In the case of mercuric and cupric sulphide sols, it is found that dilution increases the stability of the sol irrespective of the nature of the electrolyte. The effect cannot reasonably escape observation.

All these apparently anomalous facts can be explained on the assumption that distance between the particles of a sol is an important factor in determining its stability. On the adsorption theory of Freundlich, coagulation is due to the neutralisation of the charge of the particles of the sol by adsorbed cations. Other things being equal, it follows that an increase in the total surface of the colloid would mean a decrease in the surface concentration of the cation, so that a higher concentration of the electrolyte would now be necessary to neutralise the charge on the particles. The amount adsorbed is necessarily small, and its effect can only be perceptible when (a) the difference in surface is great compared with the total quantity of the electrolyte present, that is, (b) when the electrolyte concentration is sufficiently low. It is evident that for the concentrations employed in the case of salts of univalent

cations the difference in stability predicted by the adsorption theory on dilution would be negligible. The adsorption theory thus predicts that dilution of the sol will always diminish its stability, and in the limiting case of salts of univalent cations, this theoretical diminution may not be perceptible.

It has been assumed in the above discussion that the individual particles in the sol do not change in any way on dilution, and hence the total surface of the colloidal particles will decrease proportionally to the dilution of the sol.

The observed increase in stability cannot thus be explained by the adsorption theory as it stands. However, if it is considered that dilution also increases the distance between the particles of a sol, it explains easily the increase in stability observed. It may be stated here that Freundlich's adsorption theory does not contemplate any effect of the distance between colloidal particles on the stability of the sol. The increased distance somehow decreases the facility for coalescence, and thus increases its stability, as will be evident from the sequel.

Dilution thus brings into play two factors which have opposite effects on the stability of the sol. The observed increase or decrease in stability is due to the predominating influence of one over the other. The observations given in table III are instructive. In order that the difference in total surface may have a decisive effect on the stability, the quantities withdrawn by adsorption should be comparable with the total quantity of electrolyte present, that is, appreciable differences in the concentrations of the electrolyte in the bulk of the liquid should result with the different dilutions of the sol employed.

As the dilution of the electrolyte increases, the differences in total surface become more dominant in determining the stability of the sol. On the other hand, if the electrolyte concentration is kept constant, then, as the dilution of the sol increases, the total surface of the colloid decreases rapidly, and the effect of adsorption becomes counterbalanced by that of the increase in distance. This is apparent from table IV.

TABLE IV.

Sol contained 19.45 millimoles of arsenious sulphide per litre.

Electrolyte: aluminium sulphate. Dilution, $N/4000$.

| Original Sol. | Sol diluted 4 times. | Diluted 16 times. | Diluted 20 times. |
|------------------------------|---|-------------------------------|-------------------------------|
| Coagulation in 7 minutes. | Coagulates im- mediately on mixing. | Coagulation in 40 seconds. | Coagulation in 50 seconds. |

Further dilutions could not be examined, as it became increasingly difficult to follow the changes in the sol.

With mercuric and cupric sulphide sols, much higher concentrations of electrolytes are required for coagulation, and it is interesting to note that in the case of these sols dilution always increases their stability. This may be ascribed to the fact that these sols are generally poorer in colloid content and that the adsorption is much smaller in comparison with the arsenious sulphide sols used.

It should be remarked that the total surface varies directly with the dilution, whereas the mean distance between the particles varies with the cube root of the dilution.

Comparative Stability of Sols having the same Colloid Content but differing in the Degree of Dispersion.

In the foregoing, it has been assumed that on dilution the individual particles do not suffer any change. The observations of Coward (*Trans. Faraday Soc.*, 1913, **9**, 142) show that dilution does not bring about a proportionate decrease in the number of sub-microns, and that the migration velocity of the particles in an electric field changes on dilution. Young and Neal (*loc. cit.*) have also observed an increase in migration velocity on dilution with cupric sulphide sols.

In view of these observations, a comparison of a pair of sols which have the same colloid content, but differ in the degree of dispersion, was thought desirable. This is possible with arsenious sulphide sols. Such a comparison has the advantage that, in reality, two sols are compared, one of which has a smaller number of larger particles, whilst the other has a larger number of smaller particles for the same volume. A simple calculation will show that the mean distance between the particles and the total surface of the colloid in a given volume differ in the same ratio. The ratio is given by $\frac{2}{3}(n_1) : \frac{2}{3}(\overline{n_2})$, where " n_1 " and " n_2 " denote the number of particles present in each case. The relative effects of these factors can thus be compared directly. The finer sol will evidently contain a greater number of particles than the coarser one.

The results leave no doubt as to the greater stabilising effect of increased distance. Of course, here also, with dilute electrolyte solutions and sols differing greatly in the degree of dispersion, the surface effect is perceptible.

By varying the conditions of experiment, a series of sols having the same sulphide content was prepared. For comparison, the coarsest and the finest sols are selected.

TABLE V.

Electrolyte: strontium chloride.

Both sols contained 8.52 millimoles of arsenious sulphide per litre.

| Dilution. | Sol I (fine sol). | Sol II (coarse sol). |
|--------------|---|--|
| N/200 | Coagulation after a few seconds. | Coagulation after a minute. |
| N/300 | Coagulation after 2 minutes. | Coagulation after 4 minutes. |
| N/400 | Coagulation after 13 minutes. | Turbidity perceptible after 1 minute. A portion of the colloid had separated after 40 minutes. |
| N/500] | The greater portion had separated after 40 minutes. | |

It appears that the magnitude of the difference in stability is roughly the same for the different electrolytes. It will be seen from the sequel that dissolved hydrogen sulphide has an anomalous effect on the rate of coagulation of arsenious sulphide sol in the case of certain salts. Here, also, the greater stability of the coarser sol is quite marked. In table VI are given the respective concentrations of an electrolyte which corresponds with about the same coagulation time for these two sols.

TABLE VI.

| Electrolyte. | Comparable concentrations. | | Remark. |
|--------------------------|----------------------------|---------|----------------------------------|
| | Sol I. | Sol II. | |
| SrCl ₂ | N/500 | N/400 | In presence of H ₂ S. |
| " | N/400 | N/300 | |
| LiCl | N/8 | 5N/32 | |
| NH ₄ Cl | N/20 | N/16 | |
| KCl | N/20 | N/16 | |

Influence of Dissolved Hydrogen Sulphide on the Stability of Metal Sulphide Sols.

(a) Arsenious Sulphide.

In the paper referred to, it was stated that dissolved hydrogen sulphide stabilises arsenious sulphide sols against coagulation by electrolytes. The electrolytes used at that time were salts of univalent cations. It has subsequently been observed that arsenious sulphide sols behave in an anomalous manner. When solutions of

barium and strontium chlorides, magnesium sulphate, and thorium nitrate are used, the sol containing hydrogen sulphide becomes less stable. Tables VII and VIII show that the diminution in stability is as marked as the increase in stability observed with the other electrolytes. In each set of experiments, the sol and the electrolyte were both saturated with hydrogen sulphide freed from impurities. Five c.c. of each were withdrawn by means of a pipette with the help of a rubber hand pump and kept in separate test-tubes. The liquids were then mixed as usual and kept well corked with india-rubber stoppers. Care should be taken that the liquids do not touch the rubber.

TABLE VII.

Arsenious sulphide sol containing 17.58 millimoles per litre.
Electrolyte: aluminium sulphate.

| Dilution. | H ₂ S absent. | H ₂ S present. |
|--------------|---|---|
| N/24,000 ... | Complete coagulation after 2 minutes. | Partial coagulation after 3½ minutes. |
| N/30,000 ... | Partial coagulation after 6 minutes. Complete after 11 minutes. | Only slight turbidity after 21 minutes. |

TABLE VIII.

Comparable Concentrations.

| Electrolyte. | Sol I. | | Sol II. | | Sol III. | |
|---|--------------------------|---------------------------|--------------------------|---------------------------|--------------------------|---------------------------|
| | H ₂ S absent. | H ₂ S present. | H ₂ S absent. | H ₂ S present. | H ₂ S absent. | H ₂ S present. |
| KCl | N/18 | N/8 | — | — | N/16 | N/8 |
| NH ₄ Cl | N/20 | N/12 | N/20 | N/12 | N/20 | N/12 |
| BaCl ₂ | N/800 | N/1000 | N/800 | N/1000 | — | — |
| SrCl ₂ | N/300 | N/400 | N/300 | N/400 | — | — |
| Th(NO ₃) ₄ | N/10,000 | N/12,000 | — | — | — | — |

The data with thorium nitrate refer to the sol mentioned in table VII. Sols I and II are the same as those in tables V and VI. Sol III is a fine sol containing 34.8 millimoles of arsenious sulphide per litre.

The results show that the magnitude of the stabilising effect varies somewhat with the quality of the sol used. A quantitative comparison is beyond the scope of the present paper.

(b) *Mercuric Sulphide.*

Hydrogen sulphide has a similar influence on mercuric sulphide sols. Increase in stability was observed for ammonium and

potassium chlorides and a diminution for barium and strontium chlorides.

The sols were prepared as usual from the freshly precipitated hydroxide or sulphide after they had been washed free from electrolytes. The sols had a blackish-grey appearance.

The coagulation of these sols differs in one respect from that of arsenious sulphide sols, possibly due to the fact that they are comparatively poorer in sulphide content. Sols, unless very rich in sulphide, show a minimum coagulation time (as defined here); for example, a mercuric sulphide sol gave a clearance time of about two minutes from $N/20$ - to $N/300$ -barium chloride. With more dilute solutions, the coagulation time increased rapidly as usual.

(c) Cupric Sulphide.

It is well known that dissolved hydrogen sulphide markedly stabilises the pure sulphide sols both in aqueous and non-aqueous media (Lottermoser, *J. pr. Chem.*, 1907, [ii], 75, 293) and facilitates their solution. It is natural to conclude that the same protective effect would be observed with the sulphides of different metals in the presence of electrolytes. This is, however, not the case here. It has been found that hydrogen sulphide diminishes the stability of cupric sulphide sols. This holds good for all the electrolytes studied, namely, potassium, ammonium, strontium, and barium chlorides, and aluminium sulphate, and the anomaly observed with arsenious and mercuric sulphide sols is absent. Young and Neal (*loc. cit.*) could not find any perceptible effect of hydrogen sulphide on the stability. This is probably due to the method they used.

The observed diminution in stability can be understood from an observation of Young and Neal. They find that hydrogen sulphide diminishes the velocity of migration of the particles of a cupric sulphide sol in an electric field. It follows from the well-known Helmholtz-Lamb formula (*Rep. Brit. Assoc.*, 1887, 495) that a diminution of the electric charge of the particles takes place provided that other factors remain constant. The result will be a diminution in stability, as a smaller amount of adsorbed cations will now be required to discharge the particles. As it is not clear that simultaneous measurements of viscosity and other properties were made, the parallelism loses much of its significance.

Solutions of ammonium, potassium, barium, and strontium chlorides, and aluminium sulphate were studied. With ammonium and potassium chlorides, nearly saturated solutions have to be used.

TABLE IX.

| Electrolyte. | Dilution. | Clearance time. | |
|---|-----------|--------------------------|---------------------------|
| | | H ₂ S absent. | H ₂ S present. |
| KCl | — | 6 minutes. | A few seconds. |
| BaCl ₂ | N/20 | 9 " | 4 minutes. |
| Al ₂ (SO ₄) ₃ | N/2000 | 13 " | 9 " |

Protective Action of Alkali Sulphides and Alkali Hydroxides.

Solutions of potassium and sodium sulphides have a more marked protective action. This stabilising influence has been found for ammonium, potassium, barium, and strontium chlorides, and aluminium sulphate on hydrosols of cupric, mercuric, and arsenious sulphides. The behaviour of the sols is thus very regular.

This is also the case with alkali hydroxides. A trace greatly facilitates the preparation of sols rich in sulphide, and largely increases their stability. The protective action of alkali sulphides is probably due to the free alkali hydroxide present as a result of hydrolysis.

Since these substances dissolve arsenious sulphide with the formation of arsenites and thioarsenites, it is not possible in this case to refer the protective action observed to the hydroxidions alone. Indeed, the liquid obtained by dissolving in a few c.c. of dilute alkali hydroxide as much arsenious sulphide as possible has an equally marked protective action on the sols of these three sulphides. However, as alkali hydroxide does not react with the other sulphides and produces similar protective action, it is probably that the effect of all these substances is due to the trace of free alkali hydroxide present as the result of hydrolysis.

Freundlich (*Zeitsch. physikal. Chem.*, 1903, **44**, 144) has observed that salts of alkali metals with organic anions of large mass have a lower coagulating power than the corresponding salts of inorganic acids. He refers this to the protective action of these anions, due to greater adsorbability, but in view of the preceding this can as well be due to the trace of alkali hydroxide present on hydrolysis.

In conclusion, it may be stated that the anomalous influence of hydrogen sulphide is not without parallel. Recently Freundlich has found somewhat similar behaviour with ferric hydroxide hydrosol (*Biochem. Zeitsch.*, 1917, **81**, 87). An actual reversion of stability was not, however, observed in this case. So far as can be understood from the abstract of the paper, he explains these irregularities as due to selective adsorption (*loc. cit.*). It remains

to be seen how far these observations can be explained on the basis of the existing theories.

Our best thanks are due to Sir P. C. Rây and to Dr. J. C. Ghosh.

UNIVERSITY COLLEGE OF SCIENCE,
CALCUTTA.

[Received, February 4th, 1919.]

XXXVI.—*A Simple Form of Apparatus for Estimating the Oxygen Content of Air from the Upper Atmosphere.*

By FRANCIS WILLIAM ASTON.

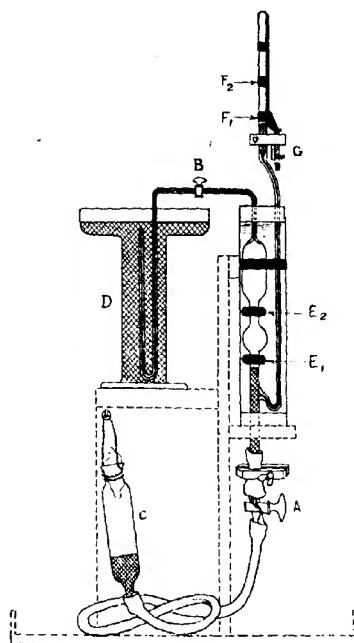
FROM meteorological considerations, it is probable that air in the stratosphere or isothermal layer is stagnant, hence, owing to their different densities, the relative percentage of oxygen and nitrogen will not be identical with that in the troposphere, where mixing is practically perfect. It is therefore of great importance that exact analyses should be made whenever possible of samples of air brought down from the great altitudes now available to aeroplanes in order to find out at what height such gravitational separation becomes evident to chemical analysis. For this purpose, it is enough to determine the oxygen content of the sample after this has been dried and freed from carbon dioxide.

A complete and exceedingly accurate method for determining the percentage of oxygen in air volumetrically has been described by Watson (T., 1911, 99, 1460). The apparatus which forms the subject of this paper is a modification of this, in which, by measuring the difference only in oxygen content between the sample and normal air, very considerable simplifications may be made, the pump and the cathetometer being rendered unnecessary.

The samples are contained in test-tubes holding rather more than is required for an analysis (10 c.c.), in the tops of which have been fused a little potassium hydroxide. Here they remain over mercury for at least two hours before analysis in order to remove carbon dioxide and water vapour.

The measuring burette and barometer tube (see figure) are normally kept full of mercury with the stopcock *A* turned on to avoid fracture by expansion. In order to perform an analysis, the capillary stopcock *B* is closed and the reservoir *C* lowered until the level of the mercury in the barometer tube is a little below its

upper and broader part. The stopcock *A* is then closed, and the sample tube held down over the inverted syphon tube in the mercury trough *D*. When the capillary stopcock *B* is now opened, the air flows into the upper part of the burette and the mercury rises again to the top of the barometer tube; in order to prevent this happening with destructive violence, the lower part of the barometer is made of capillary bore (less than 2 mm.). After waiting for a few moments for pressure and temperature to adjust



themselves, the sample tube is raised, flooding the end of the inverted syphon with mercury, the stopcock *A* is opened again, and by lowering the reservoir mercury is caused to flow through the syphon and fill the capillary tube when *B* is turned off.

It will be seen that the volume of air introduced in this way is constant, being the volume of the upper part of the barometer tube (in the actual apparatus a little less than 10 c.c.); the pressure being atmospheric plus the small difference of level between the

top of the syphon tube and the mercury in the trough, the quantity will also be approximately constant. This quantity is now accurately measured by adjusting the mercury level in the burette exactly to the lower fixed reading point, E_1 ; this can be done with the greatest nicety by bringing the mercury nearly up to the mark by manipulation of the reservoir and stopcock, and, finally (with the latter closed), squeezing the short length of rubber pressure-tubing with the screw clip provided as indicated. The volumes of the burette and barometer are such that the surface of the mercury in the latter will be somewhat as indicated in the diagram, and the lower movable reading point, F_1 , may be exactly adjusted to it by means of the micrometer screw, G .

The barometer and the parts of the burette where readings are taken are all made of the same piece of glass tube 0.9 cm. in internal diameter to eliminate meniscus error. The reading points are all sleeves of brass tube 1 cm. long fitting the glass tubes, clamped in the case of the fixed points, sliding loosely in the case of the moving ones.

The reading of the micrometer having been taken, the air is now forced into the laboratory tube. This is a quartz test-tube holding rather more than 10 c.c., to the top of which (not quite in the centre) has been fused a pellet of phosphorus. These pellets may be easily made by allowing melted phosphorus to flow from a pipette with a narrow mouth into a tall cylinder of cold water. One spherule of about 2–3 mm. in diameter should be ample, and this is introduced into the inverted quartz tube full of mercury, shaken into position, and fused into the side with a touch from a Bunsen flame. When all the air has been transferred from the burette to the quartz tube, the phosphorus is inflamed and then heated to boiling point in order to ensure the complete removal of all oxygen. Some time is allowed for the phosphoric oxide to settle, when the deoxidised air is drawn back into the burette. It was feared when the apparatus was designed that to perform this operation satisfactorily might be difficult, or even impossible, as small bubbles of air were expected to remain behind on the walls of the quartz tube, now of necessity contaminated with the products of combustion. Such bubbles are formed, but they can be dislodged by touching with the syphon tube and then washed with a little mercury into the burette.

In Watson's apparatus, the deoxidised residue was measured at the same volume as the original air, necessitating the determination of two widely different pressures. In the present one, the residue is measured at such a volume that if the air is normal the two pressures measured would be identical, so that a very small differ-

ence of pressure only need be determined. For this purpose, the upper fixed reading point, E_2 , is used, this being set once for all during the construction of the burette, so that the upper part of the burette holds exactly 79.0 per cent. of the whole. The upper movable reading point, F_2 , is also soldered to the sliding carrier at exactly the same height above the lower one as that between the fixed points. Hence it will be seen at once that for normal air the mercury at the measurement of the residue should stand at the upper movable reading point, or, if the dimensions of the apparatus are not quite correct, at a constant small distance above or below it, a correction easily determined at any time by an analysis of normal air. If, on the other hand, there is reduction in the percentage of oxygen present, the mercury will stand at a higher level, the difference being measured on the micrometer.

A decrease of oxygen from 21 per cent. to 20 per cent. corresponds with a change in height of mercury in the ratio of 79 to 80; as the normal difference between the fixed and movable reading points in the apparatus in use is 237 mm., this gives exactly 3 mm. per 1 per cent. change. The micrometer has a range of 10 mm., which is more than ample for the changes expected, and analysis should be consistent to well within one-tenth per cent. on total air, the head of the micrometer being divided in twentieths of a millimetre, corresponding with one-sixtieth per cent.

Temperature errors are minimised by the immersion of the burette and the most of the length of the barometer tube in a small water-jacket. As the time occupied in an analysis is only a few minutes, they are not likely to be serious.

The following readings of the micrometer in mm. obtained with the apparatus will serve as an example. The first set of three were obtained with pure air, which is regarded as containing 21.00 per cent. oxygen, the second with an artificial sample in which the oxygen content had been reduced, by the addition of a known quantity of deoxygenated air, to 20.42 per cent.:

| | Pure air. | | | Sample. | | |
|-----------------|-----------|------|------|---------|------|------|
| F_1 | 3.65 | 3.38 | 4.83 | 4.52 | 5.55 | 5.40 |
| F_2 | 3.39 | 3.20 | 4.55 | 6.09 | 7.21 | 7.06 |
| Diff. | 0.26 | 0.18 | 0.28 | 1.57 | 1.66 | 1.54 |
| Mean diff. | 0.24 | | | 1.59 | | |

Decrease in percentage of oxygen $\frac{1.59 + 0.24}{3} = 0.61$ giving percentage of oxygen in sample = 20.39, in good agreement with the value expected.

FARNBOROUGH.

[Received, February 26th, 1919.]

XXXVII.—*The Resolution of Hyoscine and its Components, Tropic Acid and Oscine.*

By HAROLD KING.

HYOSCINE or scopolamine, the tropyl ester of oscine, and one of the group of Solanaceous alkaloids, receives varied and extensive use in medicine, and has on that account attracted the attention of many workers both from the chemical aspect and from the medicinal.

During the last few years, the subject has acquired an additional interest and importance as a result of the recognition that oscine (or scopoline), the basic hydrolytic product, is capable of resolution into its constituents *d*- and *l*-oscine. This follows from the resolution of benzoyloscine by Tutin in 1910 (T., 97, 1793) and from the partial elucidation of the structural formula of oscine by Schmidt and Hess and their co-workers, whereby it seems certain that oscine, unlike tropine, is not internally compensated. Apart from these two separate results, and in spite of the vast amount of work that has been carried out on oscine and hyoscine, there was nothing known which definitely pointed to this conclusion. Since tropic acid is also capable of resolution, and Gadamer (*Arch. Pharm.*, 1901, 239, 294) has shown that *l*-tropic acid may be obtained by hydrolysis of *l*-hyoscine, it follows that tropyloscine (hyoscine) might exist in ten, or possibly eleven, stereoisomeric forms consisting of four optically active, four partially racemic, two fully racemic, and one double racemic compound. The problem is in some ways analogous to that presented by the ten tetrahydroquinadine-methylenecamphors obtained by Pope and Read (T., 1913, 103, 1515), but with this difference, that in the case of the hyoscines an approach is at present (apart from the rarity of the materials) not possible from the synthetic side, as hyoscine has as yet not been obtained by the esterification of oscine by tropic acid. The elucidation of the chemistry of the isomeric hyoscines and the correct allocation of the medicinal properties to be attributed to each is of considerable moment for both sciences.

Our knowledge of the hyoscines as revealed by previous workers, so far as it appertains to the present subject, may be very briefly summarised.

Naturally occurring *laevo*-hyoscine has been obtained in a state of purity by several workers, and in the form of its well-crystallised hydrobromide is a commercial product. In the plant, it is apparently accompanied to some extent by *dl*-hyoscine, from which

it can be separated by fractional crystallisation of the hydrobromides. Racemic hyoscine base, which can also be obtained from *l*-hyoscine by the action of alkalis, forms two hydrates, one crystallising with two molecules of water, and known as atroschine (Hesse), the other with one molecule of water. Two attempts to resolve racemic hyoscine are recorded, the first by Schmidt (*Arch. Pharm.*, 1898, **236**, 56), who found that the salt with thiocyanic acid did not separate into two mechanically separable crystalline enantiomorphs, as was the case with racemic lupanine (Schmidt and Davis, *Arch. Pharm.*, 1897, **235**, 196), the second by Gadamer (*Arch. Pharm.*, 1901, **239**, 294), who states that the quinic acid and *d*-mandelic acid salts of *dl*-hyoscine are very readily soluble and possess little crystallising power, and are therefore not suitable for the resolution of hyoscine.

The primary mode of attack adopted in the present investigation is based on some unpublished preliminary experiments by Tutin, who showed that *l*-hyoscine of commerce forms a soluble, deliquescent salt with *d*-bromocamphorsulphonic acid which can be recrystallised from dry ethyl acetate containing alcohol, and also that when *l*-hyoscine is racemised by alkali, the product as a salt with the same acid can likewise be recrystallised, and the successive fractions of salt so obtained show a progressive variation in rotatory power. The author here gratefully acknowledges his indebtedness to Mr. Tutin for placing these results at his disposal.

A quantity of crystalline hydrobromides of feeble levorotatory power, obtained as a by-product in the manufacture of the therapeutically valuable *l*-hyoscine, was fractionally crystallised as a salt with *d*- α -bromo- π -camphorsulphonic acid, when the first salt to be isolated was *meteloidine bromocamphorsulphonate* (m. p. 224–227°). This salt crystallises exceedingly well, and contains *meteloidine* (compare Pyman and Reynolds, T., 1908, **93**, 2077). On continuing the fractionation, *d*-hyoscine *bromocamphorsulphonate* was obtained in a state of purity. It melted at 159–160°, and crystallised in glistening, acicular needles.

d-Hyoscine hydrobromide was prepared from it, and found to crystallise with three molecules of water and to possess a specific rotatory power $[\alpha]_D +23.1^\circ$, which corresponds with a value $[\alpha]_D +33.4^\circ$ for the *d*-hyoscinium ion. For comparison, some of the maximum values recorded by previous observers for the *laevo*-salt are tabulated below.

l-Hyosine Hydrobromide.

| | $[\alpha]_D$ anhydrous salt. | $[\alpha]_D$ ionic value. |
|--|---------------------------------|------------------------------|
| Schmidt ¹ | -25.7° | -32.5° |
| Hesse ² | -25.9 | -32.7 |
| Thoms and Wentzel ³ | -25.76 | -32.5 |
| Carr and Reynolds ⁴ | -26.0 | -32.8 |
| Willstätter and Hug ⁵ | -26.0 | -32.8 |
| King ⁶ | -25.9 | -32.7 |

d-Hyosine Hydrobromide.

| | | |
|-------------------------|--------|--------|
| King ⁷ | +26.3° | +33.2° |
|-------------------------|--------|--------|

¹ *Arch. Pharm.*, 1892, 230, 207.² *J. pr. Chem.*, 1901, [ii], 64, 353.³ *Ber.*, 1901, 34, 1023.⁴ *T.*, 1910, 97, 1330.⁵ *Zeitsch. physiol. Chem.*, 1912, 79, 146.⁶ P. 504.⁷ P. 503.

These values show that the purified *l*-hyosine hydrobromide of previous workers and the *d*-hyosine hydrobromide now isolated for the first time represent one pair out of the eleven possible stereoisomeric hyoscines.

On mixing equal weights of pure *d*- and *l*-hyosine hydrobromides and recrystallising the mixture from water, *dl*-hyosine hydrobromide, also crystallising with three molecules of water and in a form indistinguishable from the active components, was obtained. It differs from the active components in that it very readily effloresces and in that the base obtained from it is crystalline and contains two molecules of water. For the further characterisation of these three related compounds, their *aurichlorides*, *auribromides*, and *picrates* were prepared. The results are shown in the following table:

| Base— | <i>l</i> -Hyosine. | <i>d</i> -Hyosine. | <i>dl</i> -Hyosine. |
|--------------------------------|----------------------------|----------------------------|---------------------------|
| Appearance | Syrup. | Syrup. | Prisms. |
| H ₂ O | — | — | 2H ₂ O |
| M. p. | — | — | 38—40° |
| Hydrobromide— | | | |
| Appearance | Large rhombic tablets. | Large rhombic tablets. | Large rhombic tablets. |
| H ₂ O | 3H ₂ O | 3H ₂ O | 3H ₂ O |
| M. p. (anhydrous) | 193—194° | 193—194° | 181—182° |
| $[\alpha]_D$ (anhydrous) | -25.9° | +26.3° | — |
| Picrate— | | | |
| Appearance | Slender matted needles. | Slender matted needles. | Needles. |
| M. p. | 187—188° | 187—188° | 173.5—174.5° |

| | <i>l</i> -Hyosine. | <i>d</i> -Hyosine. | <i>dl</i> -Hyosine. |
|---------------------------------|-------------------------------|-------------------------------|-----------------------------|
| <i>Aurichloride</i> — | | | |
| Appearance | Needles, both edges serrated. | Needles, both edges serrated. | Needles, one edge serrated. |
| M. p. | 204—205° | 204—205° | 214—215° |
| <i>Auribromide</i> ^a | | | |
| Appearance | Chocolate-red leaflets. | — | Chocolate-red leaflets. |
| M. p. | 187—188° | — | 209—210° |

Some of these call for further remark in view of the results of previous observers. The racemic base crystallising with $2H_2O$ is probably a purer form of Hesse's atrosine (*Ber.*, 1896, **29**, 1776), which melted at 36—37°, and was obtained by fractionally crystallising commercial samples of hyosine hydrobromide. It was obtained on one other occasion by Gadamer (*Arch. Pharm.*, 1898, **236**, 382), who gives the melting point 37—38°. The *dl*-hyosine hydrobromide agrees in its properties with those recorded by Hesse (*Annalen*, 1899, **309**, 75; *J. pr. Chem.*, 1901, [ii], **64**, 353).

The picrates have been recommended for identifying the mydriatic alkaloids by Carr and Reynolds (*T.*, 1912, **101**, 949), who describe *l*-hyosine and *dl*-hyosine picrates as slender, matted needles melting respectively at 180—181° and 193°. Neither of these melting points is in agreement with the results here recorded, which, however, do find support in the only two other recorded melting points of the picrates: Schmidt (*Arch. Pharm.*, 1894, **232**, 409) describes *l*-hyosine picrate as melting at 187—188°, and Finnmøre and Braithwaite (*Pharm. J.*, 1912, **89**, 136), from an examination of commercial samples of hyosine hydrobromide of varying rotatory power, give figures which show that *l*-hyosine picrate melts at 187—188° and *dl*-hyosine picrate at 174—175°.

The aurichlorides have been described by almost all previous workers on the hyoscines, but there is complete disagreement between the recorded melting points. This is all the more surprising, as several workers have had in hand pure *l*-hyosine hydrobromide. To quote only two of these, Schmidt (*Arch. Pharm.*, 1910, **248**, 641) states that *l*-hyosine aurichloride of various origins has previously been shown to melt when quite pure at 210—214°, whereas Hesse (*J. pr. Chem.*, 1901, [ii], **64**, 274) states that after many crystallisations he never found any salt to melt above 198°. The melting points now recorded for the *d*- and *l*-hyosine aurichlorides are for salts prepared in two different ways and recrystallised to constant melting point. In substantial agreement with these values, Thoms and Wentzel (*Ber.*, 1901, **34**, 1023) give 204°, and Finnmøre and Braithwaite (*loc. cit.*) record

several almost pure commercial *l*-hyoscyne hydrobromides as furnishing aurichlorides melting at 200—204°.

Tropic Acid. The Acid Constituent of Hyoscyne.

As has already been stated, Gadamer showed that *l*-hyoscyne on hydrolysis with the base tropine gave *l*-tropic acid. This crude acid, on purification by recrystallisation from water, gave *l*-tropic acid melting at 125—126°, and having a specific rotatory power in water $[\alpha]_D -71.8^\circ$. Gadamer regarded this as optically pure, since Ladenburg and Hundt (*Ber.*, 1889, **22**, 2591) record the value $[\alpha]_D +71.4^\circ$ for pure *d*-tropic acid melting at 127—128°.

Instead of employing a base for the hydrolysis, *l*-hyoscyne has now been hydrolysed by boiling with dilute hydrochloric acid, when a crude *l*-tropic acid (m. p. 125—127°, $[\alpha]_D -70.5^\circ$) was obtained, which on recrystallisation gave *l*-tropic acid melting at 127—128° and having $[\alpha]_D -76^\circ$ in water. As this rotation was numerically considerably greater than the value recorded by the aforementioned workers, it was necessary to repeat the resolution of tropic acid.

A comparison of the results obtained with those of previous investigators is shown in the following table:

| | Ladenburg and Hundt. | Amenomiya. ¹ | King. |
|--|-------------------------|-------------------------|--------------|
| <i>Quinine d-tropate—</i> | | | |
| M. p. | 186—187° | 189—190° | 191.5—192.5° |
| $[\alpha]_D$ 95 per cent. alcohol | — | — | -114° |
| <i>Quinine l-tropate—</i> | | | |
| M. p. | 178° | 184—185° | 185—186° |
| $[\alpha]_D$ 95 per cent. alcohol | — | — | -141° |
| <i>d-Tropic acid—</i> | | | |
| M. p. | 127—128° | 126—127° | 128—129° |
| $[\alpha]_D$ water | — | — | +81.6° |
| $[\alpha]_D$ alcohol | +71.4° | +71.3° | +71.8° |
| <i>l-Tropic acid—</i> | | | |
| M. p. | 123° | 126° | 128—129° |
| $[\alpha]_D$ water | — | -72.7° | -81.2° |
| $[\alpha]_D$ alcohol ... | -65.1° | — | — |

¹ *Arch. Pharm.*, 1902, **240**, 501.

It is at once seen that Ladenburg and Hundt's value $[\alpha]_D +71.4^\circ$ is the value in alcoholic solution, Gadamer having regarded it as the value in water, as the aforementioned investigators were not

very explicit, merely stating that the specific rotatory power was $+71.4^\circ$ in solutions of various concentration.

As previous workers appeared to have experienced some difficulty in obtaining pure quinine *l*-tropate from the mother liquors, a variant was made by converting the recovered partly resolved *l*-tropic acid into the quinidine salt. Further, by use of the two stereoisomeric alkaloids quinine and quinidine, but commencing the resolution with quinidine, 55 per cent. of pure quinidine *l*-tropate was first isolated, then an 80 per cent. yield of pure quinine *d*-tropate, and simultaneously a 14 per cent. yield of pure quinine *l*-tropate. On reverting to quinidine, a further 19 per cent. yield of quinidine *l*-tropate was obtained. In this way, approximately 84 per cent. of the tropic acid was resolved into its constituents. It would, however, be probably an advantage, other factors being equal, to start the resolution with quinine and follow with quinidine, since experiment showed that, starting with quinine, 66 per cent. of quinine *d*-tropate was obtained pure, and, as stated above, starting with quinidine only, 55 per cent. of quinidine *l*-tropate could be separated.

It is interesting to note that previous attempts to use quinine and quinidine for the resolution of externally compensated acids, in the above sense, have not always been successful. Whereas Fischer, Scheibler, and Groh (*Ber.*, 1910, **43**, 2022) found that in the resolution of formyl- β -alanine, quinine separated the *l*-component and quinidine the *d*-extro-, Scheibler and Wheeler (*Ber.*, 1911, **44**, 2686) found that in the resolution of *d**l*-leucine the same two alkaloids always gave the *l*-acid first. This was also the experience of McKenzie (*T.*, 1899, **75**, 969) in the resolution of mandelic acid.

Oscine. The Basic Hydrolytic Product of Hyoscine.

There are numerous instances recorded in the literature of the hydrolysis of *l*-hyoscine by alkalis, but the basic hydrolytic product, oscine, $C_8H_{13}O_2N$, was invariably found to be devoid of optical activity, even in the presence of borates or strong acids (Gadamer, *Arch. Pharm.*, 1901, **289**, 322). The only occasion on which *l*-hyoscine has been hydrolysed by acids is recorded by Hesse (*Annalen*, 1892, **271**, 100), who carried out the hydrolysis with concentrated hydrochloric acid in a sealed tube at 80–100°. This furnished the base, oscine, but there is no record of its polarimetric examination.

To decide this matter, pure *l*-hyoscine has now been hydrolysed by boiling with excess of 10 per cent. hydrobromic acid, the change

of rotation being followed polarimetrically. When hydrolysis was complete, the *l*-tropic acid was removed by extraction with ether, and the residual solution of oscine hydrobromide was found to be devoid of optical activity. As Tutin had shown that benzoyl-*d*-oscine on hydrolysis with hydrochloric acid gave *d*-oscine, the hydrolysis of *l*-hyosicine was repeated, using hydrochloric acid. Again the oscine hydrochloride solution was inactive. As it was conceivable that the benzoylation of oscine might have effected some fundamental change in the configuration of oscine, whereby the benzoylated product became externally compensated, and therefore capable of resolution, it was necessary to prove that oscine itself could be resolved into its constituents, *d*- and *l*-oscine.

Several salts of oscine with optically active acids were prepared and examined. The salt with Reyckler's camphorsulphonic acid was not obtained crystalline, but with *d*- α -bromo- π -camphorsulphonic acid a markedly crystalline salt was obtained, which melted at 232–233°. This salt, however, proved to be a partial racemate. With *d*- α -bromo- β -camphorsulphonic acid, a very readily soluble, crystalline salt was isolated, but beyond recording a single rotation, it was not followed further, as *d*-tartaric acid was found to be eminently suitable for the resolution of oscine.

The separation of *dl*-oscine into its two pure enantiomorphs can be effected by use of *d*-tartaric acid alone, the acid salts being used for this purpose in aqueous solution. The more sparingly soluble salt, which separated almost pure after two crystallisations, is *l*-oscine *d*-hydrogen tartrate monohydrate (m. p. 173–174°, anhydrous), which crystallises magnificently in clear tablets or octahedra. Employing 14 grams of oscine in combination with a like quantity of *d*-tartaric acid, between 70 and 80 per cent. of this component was separated with no great difficulty. The *d*-oscine *d*-hydrogen tartrate contained in the mother liquors can be obtained pure either by isolation as the monohydrate, a very readily soluble, metastable salt melting below 100°, or, preferably, as the stable anhydrous salt (m. p. 167–168°). The proportion of this salt obtained in a state of purity is largely a function of time, as it crystallises very slowly, but uncommonly well, in hexagonal-shaped tablets from the cold, syrupy mother liquors.

l-Oscine picrate, hydrochloride, and base were obtained without bringing into contact with alkali at any stage, but this was found afterwards to be an unnecessary precaution, as *l*-oscine is not racemised by boiling with 10 per cent. acid or alkali, and only partly by saturated baryta at 150°.

d-Oscine picrate, hydrochloride, and base were prepared in the usual manner by liberating the base from the hydrogen tartrate

by a strong alkali. The properties of these salts as compared with the *dl*-oscine salts are shown in the following table:

| | <i>d</i> -Oscine. | <i>l</i> -Oscine. | <i>dl</i> -Oscine. |
|--|--|--|---|
| <i>Base</i> — | | | |
| Appearance | Needles. | Needles. | Needles or tablets. |
| M. p. | 109—110° | 109—110° | 109—110° |
| $[\alpha]_D$ water | +54.8° | —52.4° | — |
| <i>Picrate</i> — | | | |
| Appearance | Dimorphous rhombs and needles. | Dimorphous rhombs and needles. | Flattened rhombs. |
| M. p. | 237—238° | 237—238° | 237—238° |
| <i>Hydrochloride</i> — | | | |
| Appearance | Warts composed of prisms. Very deliquescent. | Warts composed of prisms. Very deliquescent. | Warts composed of prisms (anhydrous). Tablets (hydrated). |
| M. p. | 273—274° | 273—274° | 273—274° |
| $[\alpha]_D$ in water of basic ion | +24.0° | —24.2° | — |

It is noteworthy that the active and *dl*-isomerides have the same melting points, and mixtures of the active with the *dl* show no depression of the melting point. In the case of the bases, the melting-point curve is thus of the same type as is found for the camphoroximes.

By hydrolysis of benzoyl-*d*-oscine, Tutin (*loc. cit.*) obtained a value for the *d*-oscinium ion of $[\alpha]_D + 129^\circ$,* which he regarded as only approximate. As this was very different from the value recorded above, it was necessary to repeat the resolution of benzoyl-oscine. Pure benzoyl-*d*-oscine hydrochloride was obtained having a value $[\alpha]_D + 13.4^\circ$ for the benzoyl-*d*-oscinium ion, in agreement with the value $+12.9^\circ$ calculated from the rotation of the bromo-camphorsulphonate. This hydrochloride was submitted to hydrolysis by acids and alkalis. In both cases the result was the same, a solution being obtained which, on removal of benzoic acid, gave values $[\alpha]_D + 26.0^\circ$ and $[\alpha]_D + 25.8^\circ$, by acid and alkali hydrolysis respectively, for the *d*-oscinium ion. Moreover, the hydrochloride and picrate were isolated from the product of acid hydrolysis, and the properties were in agreement with the *d*-oscine salts obtained by the tartaric acid resolution of oscine.

Interpretation of Results.

The question now arises, which of the eight possible optically active stereoisomeric hyoscines do *d*- and *l*-hyoscine represent?

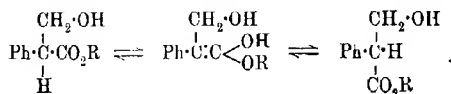
* Tutin gives the value $+77.7^\circ$, having overlooked the loss of the benzoyl group.

The various possibilities are shown in the following table, the centre column representing optically pure forms, which, combined, as shown by the arrows, yield partially racemic forms:

| Partial racemates. | Optically pure forms. | Partial racemates. |
|--|---------------------------------------|--|
| | 1. <i>l</i> -tropyl- <i>d</i> -oscine | |
| 5. <i>dl</i> -tropyl- <i>d</i> -oscine | 2. <i>l</i> -tropyl- <i>l</i> -oscine | 7. <i>l</i> -tropyl- <i>dl</i> -oscine |
| | 3. <i>d</i> -tropyl- <i>d</i> -oscine | |
| 6. <i>dl</i> -tropyl- <i>l</i> -oscine | 4. <i>d</i> -tropyl- <i>l</i> -oscine | 8. <i>d</i> -tropyl- <i>dl</i> -oscine |

Of these, 1 to 6 are at once excluded, since *l*-hyoscyne on hydrolysis with acid or alkali gives *l*-tropic acid and *dl*-oscine, whereas benzoyl *d*-oscine under similar conditions yields optically pure *d*-oscine. On these grounds, *l*- and *d*-hyoscyne, represented by 7 and 8, are therefore partially racemic esters, *l*-hyoscyne being a molecular combination of *l*-tropyl-*d*-oscine and *l*-tropyl-*l*-oscine, whilst *d*-hyoscyne is a similar combination of *d*-tropyl-*d*-oscine and *d*-tropyl-*l*-oscine.

The known inactivation of *l*-hyoscyne by alkalis would, on this basis, simply consist in the change of configuration of the tropanyl portion of the molecule, probably through the intermediary of the



enolic form, and each constituent ester of the partial racemate should give rise to a new ester.

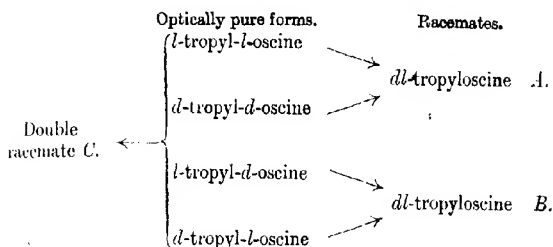
In support of this, some work, which is reserved for future publication, on the re-resolution of racemised *d*-hyoscyne has resulted in the isolation of two esters only, *d*- and *l*-hyoscyne, which is not surprising, as these, being partial racemates, would contain the four expected optically pure forms.

As opposed to the partial racemic ester nature of *d*- and *l*-hyoscines may be cited the rarity of the occurrence of partial racemates in nature, and the novel behaviour of the hyoscines towards *d*-bromocamphorsulphonic acid, which, so far as *d*-hyoscyne is concerned, only resolves *dl* or weakly active hyoscyne as far as the partially racemic ester stage. Although this behaviour is, as far as it has been possible to ascertain, unique, it is only necessary to

recall that in the early days of the application of Pasteur's methods of resolution the formation of partially racemic salts was only rarely observed, whereas at the present time it is recognised as of very frequent occurrence.

At the present stage of the investigation there seem to be only two other possible alternatives, both of which appear rather remote. In the first place, *d*- and *l*-hyoscines may be optically pure forms which, owing to some specific effect of the troyl group, yield *dl*-oscine on hydrolysis, or, secondly, oscine may possess a different configuration in the troyl ester from that in the benzoyl ester and in the free state, whereby the troyl group is attached to an internally compensated ψ -oscine, which, on hydrolysis, gives rise to a resolvable oscine.

dl-Hyoscine raises a further difficulty, for there are three possible *dl*-hyoscines, as is shown by the following arrangement:



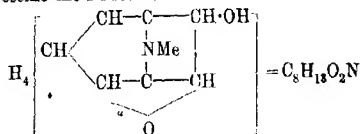
The optically pure forms may be combined in pairs, as indicated, to form two different simple racemates, A and B, or all four forms may be combined to form a double racemate, C. On the acceptance of the partial racemic ester nature of *d*- and *l*-hyoscines, *dl*-hyoscine hydrobromide crystallising with three molecules of water, and obtained by crystallising together equal weights of *d*- and *l*-hyoscine hydrobromides, constitutes a double racemic salt, the absence of any indication of the presence of another salt and the identical crystalline appearance of *d*- or *l*-hyoscine hydrobromide and this salt supporting this view. Moreover, the base crystallising with $2\text{H}_2\text{O}$ is the base contained in this *dl*-salt, as both give the same picrate.

As has already been indicated in the opening paragraph, there is another hydrate of racemic hyoscine base, containing $1\text{H}_2\text{O}$ and melting at $56-57^\circ$. It was first obtained by Schmidt (*Arch. Pharm.*, 1894, **232**, 409), was re-examined by Luboldt (*ibid.*, 1898, **236**, 11), and more fully investigated by Gadamer (*ibid.*, 382). The last-named investigator showed that the dihydrate can readily

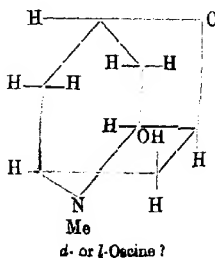
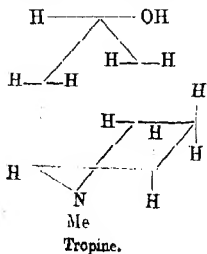
be converted into the monohydrate, but the reverse change was only effected with difficulty. Both hydrates were afterwards described by Hesse (*J. pr. Chem.*, 1901, [ii], **64**, 353), who could not substantiate Gadamer's claims. In reply, Kunz-Krause (*ibid.*, 1901, [ii], **64**, 569) examined Gadamer's three-year-old specimens, and the dihydrate had in every case changed into the base (m. p. 54–55°).

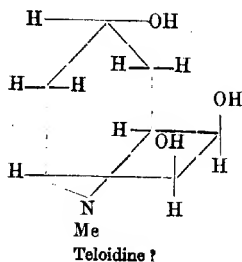
The author has not, so far, been successful in obtaining this monohydrate, so is unable to state with certainty what is the relation between these two racemic hydrates from the point of view of the partial racemic ester nature of *d*- and *l*-hyosine.

The bearing of these results on the structural formula of oscine deserves a passing notice. The most recent and most complete formula is that put forward by Hess (*Ber.*, 1918, **51**, 1007), who ascribes to oscine the structure

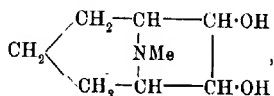


where the linking *a* is regarded as being probably attached to one of the carbon atoms of the piperidine nucleus. The experiments on the stability of the active oscines towards racemising agents certainly support this linking. Pyman and Reynolds (T., 1908, **98**, 2077) have pointed out the close relationship which exists between tropine, oscine, and teloidine, all of which contain eight carbon atoms and a hydroxyl group in the molecule. Moreover, their acyl derivatives are found together in *Datura meteloides*. The author is tempted to make the suggestion that, like tropine, the oxygen atom in question in oscine is attached to the γ -position in the piperidine ring. Oscine would therefore be the internal anhydride of a trihydroxytropine, and this trihydroxytropine may be teloidine. The formulæ suggested are:





Teloidine would thus be internally compensated, and in support of this view may be cited the occurrence of meteloidine (tiglyl-teloidine), in nature devoid of optical activity, and the non-resolution of meteloidine by bromocamphorsulphonic acid. Further, Hess (*loc. cit.*) observed that dihydro-oscine, which undoubtedly has the formula



readily produces a silver mirror when treated with ammoniacal silver nitrate solution. The author finds that teloidine and meteloidine, unlike oscine, also readily reproduce this characteristic of dihydro-oscine, the reducing property being probably associated with the adjacent hydroxyl groups, as is found in tartaric acid.

EXPERIMENTAL.

Resolution of Tropic Acid.

With Quinine.—Following the method described by Ladenburg and Hundt (*Ber.*, 1889, **22**, 2591), tropic acid (25 grams) was neutralised to litmus with quinine base (48.8 grams anhydrous) in hot 50 per cent. alcohol. A 49 per cent. yield of a quinine tropate separated. It melted at 176–179°, and had $[\alpha]_D -126^\circ$ in 95 per cent. alcohol ($c=1$). For further purification it was recrystallised from 95 per cent. alcohol, and, after five crystallisations, 17 grams of quinine *d*-tropate were obtained pure. By working once more through the mother liquors, a further 7.4 grams of pure salt were obtained without difficulty. These two separations combined represent 66 per cent. of the dextro-component.

Quinine *d*-tropate crystallises from 8 parts of boiling alcohol in

groups of radiating needles. In water it is very sparingly soluble. It melts at $191.5\text{--}192.5^\circ$ ($195.5\text{--}196.5^\circ$ corr.):

0.1035, dried at 100° , gave 0.2706 CO_2 and 0.0633 H_2O .

$\text{C}=71.3$; $\text{H}=6.8$.

$\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2\text{C}_9\text{H}_{10}\text{O}_3$ requires $\text{C}=71.0$; $\text{H}=7.0$ per cent.

The specific rotation was determined in 95 per cent. alcohol.

$c=1.01$; $l=2\text{-dm.}$; $\alpha_D - 2^\circ 18'$; $[\alpha]_D - 113.8^\circ$.

In absolute alcohol the rotation is smaller.

$c=1.013$; $l=2\text{-dm.}$; $\alpha_D - 2^\circ 6.4'$; $[\alpha]_D - 104.0^\circ$.

$c=1.002$; $l=2\text{-dm.}$; $\alpha_D - 2^\circ 5.4'$; $[\alpha]_D - 104.3^\circ$.

As previous observers appeared to have experienced some difficulty in obtaining quinine *l*-tropate in a state of purity, no attempt was made at this stage to isolate this salt. The mother liquors were therefore combined, and the tropic acid containing excess of the *l*-*vo*-component was recovered. Small test samples were converted into the neutral salts with brucine, cinchonine, and quinidine, but although the two former gave crystalline salts, the crystallising power of these was not so pronounced as the salt with quinidine. Accordingly, 3.5 grams of this partly resolved tropic acid were crystallised as quinidine salt, when 4.2 grams of quinidine *l*-tropate were obtained of constant specific rotatory power.

Resolution with Quinidine and Quinine.—*dl*-Tropic acid (15 grams) was neutralised with quinidine dissolved in 50 c.c. of 95 per cent. alcohol. On keeping, 22 grams of crystalline material separated. It was obviously a mixture, and had $[\alpha]_D + 151^\circ$ in 95 per cent. alcohol ($c=2$). After four crystallisations, the specific rotation was constant at $[\alpha]_D + 145^\circ$, and the collected quinidine *l*-tropate amounted to 5.5 grams.

Quinidine *l*-tropate crystallises from 95 per cent. alcohol, in which it is soluble in its own weight at 80° , in clusters of well-formed, stout, transparent prisms containing one molecule of water. These exhibit a pronounced heliotrope triboluminescence when powdered in the dark. The air-dried salt when heated in a capillary tube shrinks from about 110° , liquefies between 118° and 120° , and effervesces at 124° . When, however, it is exposed on a watch-glass to a temperature of 90° , it melts completely, and crystallises again on addition of alcohol:

0.2038, air-dried, lost 0.0069 at 100° . $\text{H}_2\text{O}=3.4$.

0.1029 " gave 0.2590 CO_2 and 0.0672 H_2O . $\text{C}=68.7$;

$\text{H}=7.3$.

$\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2\text{C}_9\text{H}_{10}\text{O}_3\cdot\text{H}_2\text{O}$ requires $\text{H}_2\text{O}=3.5$; $\text{C}=68.5$; $\text{H}=7.1$ per cent.

Its specific rotation was determined in 95 per cent. alcohol, and is dependent on the concentration.

$$c=0.979; l=2\text{-dm.}; \alpha_D + 2^{\circ}55.2'; [\alpha]_D + 149.1^{\circ}.$$

$$c=1.995; l=2\text{-dm.}; \alpha_D + 5^{\circ}46.5'; [\alpha]_D + 144.7^{\circ}.$$

The mother liquors were worked up further, and gave an additional 7.2 grams, $[\alpha]_D + 146^{\circ}$. This is approximately a 55 per cent. yield of quinidine *l*-tropate. As the liquors now showed no tendency to crystallise at all readily, they were combined, and the tropic acid was recovered by use of ether and hydrochloric acid (10 per cent.). On now crystallising as the quinine salt, after three crystallisations, 14.8 grams of quinine *d*-tropate were obtained pure, $[\alpha]_D - 114^{\circ}$ ($c=1$), and a further 2.8 grams with $[\alpha]_D - 115^{\circ}$. The first mother liquors on concentration deposited quinine *l*-tropate as a homogeneous crop (4.8 grams) of glistening, triangular plates having $[\alpha]_D - 139^{\circ}$, and melting at $184-185^{\circ}$. It was recrystallised twice from 95 per cent. alcohol, the specific rotation remaining constant at $[\alpha]_D - 140.7^{\circ}$ and the melting point at $185-186^{\circ}$, but the form of the crystals changed to needles very similar in appearance to quinine *d*-tropate.

Quinine *l*-tropate melts at $185-186^{\circ}$ ($189-190^{\circ}$ corr.). It is very much more readily soluble in hot alcohol than is quinine *d*-tropate. The diverse crystalline forms described above do not constitute a case of dimorphism, but merely represent extreme crystalline forms. By suitably modifying the conditions of crystallisation, a series of intermediate forms may be obtained consisting of more or less elongated trapezoidal plates. Unlike quinine *d*-tropate, this salt exhibits a very faint triboluminescence, the intensity of which is not visibly affected by the form of the crystals:

0.1083, dried at 100° , gave 0.2817 CO_2 and 0.0668 H_2O .

$\text{C}=71.0; \text{H}=6.9.$

$\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2, \text{C}_7\text{H}_{10}\text{O}_3$ requires $\text{C}=71.0; \text{H}=7.0$ per cent.

The tropic acid contained in the residual liquors was reconverted into the quinidine salt, when 4.3 grams of quinidine *l*-tropate were obtained, having $[\alpha]_D + 145^{\circ}$. The residual solution was not further examined.

By the use of the two bases quinidine and quinine, there were thus isolated in an approximate state of purity 88 per cent. of quinine and quinidine *l*-tropates and 80 per cent. of quinine *d*-tropate. The proportion of tropic acid resolved is 84 per cent.

Quinidine *d*-tropate was not isolated, but, on keeping in the ice-chest, a small crop of white, woolly needles separated from the

mother liquors (together with quinidine *l*-tropate), which was probably this salt in an impure condition.

d-Tropic Acid.

Pure quinine *d*-tropate (16 grams) was acidified with 50 c.c. of 5 per cent. hydrochloric acid and completely extracted with purified ether. The crude acid so obtained (5.1 grams) melted at 127—128°, and had $[\alpha]_D + 77.2^\circ$ in water ($c=1$). On recrystallisation from water, the melting point rose to 128—129°, and the rotation to $[\alpha]_D + 79^\circ$. After two more crystallisations, the melting point remained unchanged, but the rotation rose to $[\alpha]_D + 81.6^\circ$. The yield was 3.1 grams.

d-Tropic acid crystallises from water in delicate, lustrous scales, which become transformed on keeping in contact with the solution into elongated prisms of hexagonal cross-section. Both forms melt at 128—129° (129—130° corr.) and are anhydrous:

0.2014 was equivalent to 11.9 c.c. *N*/10-baryta.

M.W.=169. $C_9H_{10}O_3$ requires M.W.=166.

The specific rotation was determined in alcohol and in water.

In water:

$$c=1.027; l=2\text{-dm.}; \alpha_D + 1^\circ 40' 6''; [\alpha]_D + 81.6^\circ.$$

In absolute alcohol:

$$c=0.997; l=2\text{-dm.}; \alpha_D + 1^\circ 24' 2''; [\alpha]_D + 70.3^\circ.$$

$$c=2.472; l=2\text{-dm.}; \alpha_D + 3^\circ 33' 1''; [\alpha]_D + 71.8^\circ.$$

The specific rotation of the ion was determined by dissolving 0.200 gram of *d*-tropic acid and 0.0638 gram of anhydrous sodium carbonate in water and making up to 20 c.c. The dissolved carbon dioxide was not removed:

$$l=2\text{-dm.}; \alpha + 1^\circ 22' 9''; [\alpha]_D \text{ for ion} + 69.4^\circ; [M]_D \text{ for ion} + 114.7^\circ.$$

Gadamer (*Arch. Pharm.*, 1901, **239**, 294) has previously noted a fall of rotation of *l*-tropic acid on converting into a salt, but has not followed it quantitatively.

l-Tropic Acid.

From Quinidine l-Tropate.—Four grams of pure quinidine *l*-tropate, on treatment with hydrochloric acid (10 per cent.) and extraction with ether, gave 1.35 grams of *l*-tropic acid, which, after three crystallisations from water, gave 0.5 gram melting at 128—129° (129—130° corr.). The specific rotatory power was determined in water, and was slightly less than that of the purest *d*-tropic acid:

$$c=0.995; l=2\text{-dm.}; \alpha_D - 1^\circ 37'; [\alpha]_D - 81.2^\circ.$$

From Quinine l-Tropate.—5.8 Grams of this salt gave 2.0 grams of *l*-tropic acid, which was recrystallised four times from water, giving 1.35 grams melting at 128–129°, and with a specific rotation -81.2° :

$$c=1.002; l=2\text{-dm.}; \alpha_D - 1^\circ 37.6'; [\alpha]_D - 81.2^\circ.$$

l-Tropic acid prepared in this way had the same general properties as the dextro-acid. It is very sparingly soluble in cold benzene, but freely so in cold methyl ethyl ketone or ethyl acetate. From the latter solvent, it crystallises exceedingly well in clear tablets:

0.1975 was equivalent to 11.72 c.c. *N*/10-baryta.

M.W.=168. $C_9H_{10}O_3$ requires M.W.=166.

The Resolution of Oscine.

Partial Racemate with d- α -Bromo- π -camphorsulphonic Acid.—

Two and a-half grams of oscine were converted into this salt, which was very conveniently recrystallised from absolute alcohol. The first crop of crystals weighed 4.9 grams, melted at 232°, and gave $[\alpha]_D + 58.8^\circ$ in water ($c=2$). It was recrystallised twice more from absolute alcohol, yielding, finally, 3.6 grams melting at 232–233°. The specific rotation determined in water was practically unchanged:

$$c=2.001; l=2\text{-dm.}; \alpha_D + 2^\circ 22.4'; [\alpha]_D + 59.3^\circ; [M]_D + 276.7^\circ.$$

The value for the molecular rotation 276.7° is in good agreement with the molecular ionic value 278.7 for bromocamphorsulphonic acid (Pope and Read, T., 1910, 97, 2200).

dl-Oscine d- α -bromo- π -camphorsulphonate crystallises exceedingly well from absolute alcohol in clear, diamond-shaped plates. Ten parts by volume of boiling absolute alcohol are required to dissolve one part by weight of the salt. It melts at 232–233° (237–238° corr.):

0.0995, dried at 100°, gave 0.1703 CO_2 and 0.0526 H_2O .

C=46.69; H=5.91.

$C_9H_{13}O_2N, C_{10}H_{15}O, BrS$ requires C=46.34; H=6.05 per cent.

Behaviour with d- α -Bromo- β -camphorsulphonic Acid.—Six and a-half grams of oscine were combined with an equivalent of *d- α -bromo- β -camphorsulphonic acid*. The salt could not be obtained crystalline either from water or from a mixture of ethyl acetate and absolute alcohol. A very concentrated solution of the salt in absolute alcohol, however, crystallised as a cake of needles on keeping for a prolonged time in the ice-chest. It was too readily soluble for systematic fractionation from absolute alcohol, and the addition of dry ethyl acetate unexpectedly prevented crystallisa-

tion. The first crop of crystals from absolute alcohol was collected, and weighed 8.7 grams. It melted at 150–155°, and its specific rotation was determined in water:

$$c=2.00; l=2\text{-dm.}; \alpha_D + 2^{\circ}27'4''; [\alpha]_D + 61.4^{\circ}; [M]_D + 286.3^{\circ}.$$

This product was recrystallised from absolute alcohol, but in the meantime tartaric acid had effected the resolution of oscine quite simply, so the investigation of the above salt was discontinued.

With Camphor- β -sulphonic Acid.—Attempts to crystallise this salt were ineffective.

Resolution by d-Tartaric Acid.—*dl*-Oscine (13.9 grams) was converted into its *d*-hydrogen tartrate by addition of 13.5 grams of *d*-tartaric acid in aqueous solution. The solution was concentrated to a low bulk, and gave 13.8 grams of a salt crystallising in hexagonal plates and with a specific rotation $[\alpha]_D + 3.5^{\circ}$ in water. After one more crystallisation, it gave 10.2 grams and had $[\alpha]_D + 1.1^{\circ}$. This value was not appreciably altered by subsequent repeated crystallisation, and represents the optical constant of the salt *l*-oscine *d*-hydrogen tartrate.

l-Oscine *d*-hydrogen tartrate crystallises with one molecule of water of crystallisation in large and clear octahedra. Very often these have a flattened appearance, and, more rarely, one-half the faces may be almost entirely suppressed, with the formation of tetrahedra. Unbroken crystals melt at 134° with effervescence, but when powdered partly melt at about 130° and gradually liquefy up to 160°. The anhydrous material melts at 173–174° (176.5–177.5° corr.). It is readily soluble in cold water, but the crystals can be washed with 50 per cent. alcohol with little loss. From dilute alcoholic solutions, this salt tends to separate as an oil:

0.3126, dried at 105°, lost 0.0181. $H_2O=5.8$.

$C_8H_{13}O_2N, C_4H_6O_6, H_2O$ requires $H_2O=5.6$ per cent.

0.1159, dried at 100°, gave 0.1996 CO_2 and 0.0690 H_2O .

$C=47.0$; $H=6.7$.

$C_8H_{13}O_2N, C_4H_6O_6$ requires $C=47.2$ $H=6.3$ per cent.

The specific rotation was determined in water:

$$c=2.007; l=2\text{-dm.}; \alpha_D + 2^{\circ}56'; [\alpha]_D + 1.06^{\circ}.$$

The average value, for nine different samples of the pure salt, of $[\alpha]_D$ was $+1.29^{\circ}$, the extremes being $+0.93^{\circ}$ and $+1.56^{\circ}$. Taking this average value for $[\alpha]_D$, the molecular rotation $[M]_D$ is calculated as $+4.18^{\circ}$, and employing Landolt's value (*Ber.*, 1873, 6, 1075) for the molecular rotation of ammonium hydrogen tartrate,

+42.84°, the value for the *l*-oscinium ion is $[M]_D - 38.66^\circ$, whence $[\alpha]_D - 24.7^\circ$.

On continuing the fractionation of the mother liquors, 71 per cent. of the *l*-oscine *d*-hydrogen tartrate present was isolated in a state of purity. The separation was materially accelerated by inoculation of the less mobile solutions, followed by addition of alcohol in insufficient amount to precipitate an oil. The residual solutions, now relatively rich in *d*-oscine *d*-hydrogen tartrate, were concentrated to a syrup, and, on allowing to remain in a desiccator exposed to a dehydrating agent, crystallised as a striated mass of crystals. These were collected, freed from the adhering syrupy mother liquor, first by suction and then by very limited use of 50 per cent. alcohol as a washing agent. The salt was a monohydrate, and gave $[\alpha]_D + 23.7^\circ$. It was recrystallised from water, and separated under similar conditions as a felted mass of needles. These now gave $[\alpha]_D + 27.3^\circ$ (anhydrous).

d-Oscine *d*-hydrogen tartrate monohydrate melts from 55° to 65°, forming a méniscus at the latter temperature. It readily effloresces when exposed to the atmosphere, and when dehydrated in a vacuum over sulphuric acid loses its water of crystallisation. The anhydrous material still melts at 55–65°. This is probably the melting point of an amorphous form, as, on keeping, it acquires the melting point of the crystalline anhydrous salt, namely, 163–165° (see below).

Three different samples of the salt were analysed for their water content. The first, representing a freshly collected salt, gave the following result:

0.4502, dried over H_2SO_4 , lost 0.0320. $H_2O = 7.1$;

and a salt which showed some signs of efflorescence gave the following:

0.2023 lost 0.0091. $H_2O = 4.5$.

$C_8H_{13}O_2N, C_4H_6O_6, H_2O$ requires $H_2O = 5.6$ per cent.

On keeping for some time, this salt had completely effloresced:

0.1180, dried at 100°, lost nil.

0.1180, dried at 100°, gave 0.2055 CO_2 and 0.0649 H_2O .

$C = 47.5$; $H = 6.15$.

$C_8H_{13}O_2N, C_4H_6O_6$ requires $C = 47.2$; $H = 6.3$ per cent.

The specific rotation of the dehydrated salt was determined in water:

$c = 0.949$; $l = 2$ -dm.; $\alpha_D + 31.1'$; $[\alpha]_D + 27.3^\circ$.

When the hydrated salt is washed with absolute alcohol, it is transformed into a white, crystalline powder, which is the

anhydrous salt and the stable form at the ordinary temperature. When crystallised from water, the anhydrous salt separates from a syrupy solution very slowly in large, hexagonal-shaped tablets, which, unlike the hydrated salt, can be washed freely with 50 per cent. alcohol. If a syrupy solution is inoculated with a trace of both forms, hydrated and anhydrous, the hydrated form crystallises first, filling the liquid space, and, on keeping, disappears entirely, being replaced by the stable, anhydrous form. For the isolation of pure *d*-oscine *d*-hydrogen tartrate, the latter form is the more convenient. The process is, however, very slow, owing to the solubility of *d*-oscine *d*-hydrogen tartrate and the slow velocity of crystallisation from viscous solutions.

d-Oscine *d*-hydrogen tartrate melts at 167–168° (170–171° corr.).

The specific rotation was determined in water and for a salt which had been crystallised to constant rotation:

$$c=1.016; l=2\text{-dm.}; [\alpha] + 34'; [\alpha]_D + 27.87^\circ; [M]_D + 85.17^\circ.$$

This gives a value $+42.3^\circ$ for the molecular rotation of the *d*-oscinium ion and $[\alpha] + 27.10^\circ$. This is somewhat greater numerically than the value $[\alpha]_D - 24.7$ obtained by a similar calculation for the *l*-oscinium ion. As this is beyond the limits of experimental error, it is probably another example of the phenomenon first drawn attention to by Pope and Read (T., 1912, 101, 760), who show conclusively that the molecular rotatory power in aqueous solution of certain salts of the type *l*-base *d*-acid is in agreement with the value calculated from the separate ions, but that the combination *d*-base *d*-acid gives an abnormal value.

l-Oscine Picrate.—Six grams of pure *l*-oscine *d*-hydrogen tartrate were added to a boiling saturated solution of 4.25 grams of picric acid in 80 c.c. of water. As the solution cooled, the major portion of the salt crystallised in long needles, but when only luke-warm a denser form appeared in the shape of small, modified rhombs. The yield was 6.35 grams and the melting point 237° (decomp.). The combined product was recrystallised from 35 c.c. of hot water, and, on removing the source of heat, separated at once in long, glistening needles. These were collected while the solution was still warm, the filtrate continuing to deposit solely needles for some time, and then rhombs. The filtrate was heated to dissolve all the crystals, and when cold only deposited the rhomb-like form of crystal, which closely resembles *dl*-oscine picrate. The yield of needles was 4.95 grams, melting at $237\text{--}238^\circ$ (decomp.) ($242.5\text{--}243.5^\circ$ corr.), whilst the rhombs amounted to 0.95 gram, and also melted at $237\text{--}238^\circ$ (decomp.). Both forms are

anhydrous, and either form when mixed with *dl*-oscine picrate, which itself also melts at 237–238°, shows no depression of the melting point. At the ordinary temperature, the needle form of picrate is certainly the unstable one, as is readily shown by adding a drop of saturated picric acid solution to a few small crystals of *l*-oscine *d*-hydrogen tartrate and rubbing with a glass rod. The crystals dissolve instantly, and a homogeneous crop of needles first makes its appearance, followed quickly by minute rhombs, and in a short time the needles will have entirely disappeared, their disintegration and solution being readily followed with the aid of a microscope. This behaviour is useful as a test as to whether one is dealing with active or *dl*-oscine salts, since *dl*-oscine picrate has always been observed to separate in small, flattened rhombs.

l-Oscine Hydrochloride.—Four grams of *l*-oscine picrate (needle form) were decomposed by shaking with three molecular proportions of 5 per cent. hydrochloric acid, and the picric acid was removed by ether. The solution of the *l*-oscine hydrochloride was completely dehydrated by repeated evaporation to dryness with absolute alcohol, leaving, finally, a white, crystalline powder, which was dissolved in 10 c.c. of boiling absolute alcohol. On keeping, *l*-oscine hydrochloride separated in aggregates of small prisms in the form of warts; a few isolated prisms were also present. The product was collected, and amounted to 1.4 grams. It melted and decomposed at 273–274° (281–282° corr.). A mixture with *dl*-oscine hydrochloride (m. p. 273–274°) also melted at the same temperature. Unlike *dl*-oscine hydrochloride, the *laevo*-salt is very highly deliquescent. A direct comparison of the two was made by exposing a few crystals of each on watch-glasses to the atmosphere. In a few minutes, the *laevo*-salt had completely liquefied, whilst the *dl*-salt was apparently unaffected. On keeping for an hour, however, the latter showed signs of deliquescence, and the deliquesced salt recrystallised in well-formed tablets melting partly at about 30°, and probably representing the monohydrated *dl*-oscine hydrochloride described by Luboldt (*Arch. Pharm.*, 1898, **236**, 18).

The specific rotation of *l*-oscine hydrochloride was determined in water, employing a salt which had been dried at 100°:

$c = 0.997$; $l = 2$ -dcm.; $\alpha = -23.6'$; $[\alpha]_D - 19.71^\circ$; $[M]_D - 37.76^\circ$;

whence $[\alpha]_D$ for the *l*-oscinium ion is -24.2° , whereas the value calculated from the molecular rotation of *l*-oscine *d*-hydrogen tartrate was -24.7° .

l-Oscine Hydrochloride from *l*-Oscine Picrate (Rhombs).—As has been indicated above, *dl*-oscine picrate and *l*-oscine picrate melt at the same temperature, and the stable modification of

l-oscine picrate crystallises very similarly to *dl*-oscine picrate. It was therefore necessary to prove that this stable form of *l*-oscine picrate did actually contain the active base. Accordingly, 0.5 gram of *l*-oscine picrate (rhombs) was converted as quantitatively as possible by means of ether and three molecular proportions of *N*/10-hydrochloric acid into *l*-oscine hydrochloride. The solution was concentrated somewhat and made up to 20 c.c. In a 2-dcm. tube the observed rotation was $\alpha_D -25.3'$, from which it is calculated that the *l*-oscinium ion has $[\alpha]_D -21^\circ$, a value in good agreement with that observed directly for *l*-oscinium hydrochloride. The solution was then dried, and the hydrochloride recrystallised from alcohol. It gave 0.11 gram of highly deliquescent *l*-oscine hydrochloride melting at $271-272^\circ$, and when tested with saturated picric acid solution gave the unstable needle form of *l*-oscine picrate, changing into rhombs.

l-Oscine Base.—To avoid the action of alkalis, which it was thought might cause partial racemisation, *l*-oscine base was prepared as follows. *l*-Oscine picrate (4.75 grams) was treated with three equivalents of dilute sulphuric acid solution, and the picric acid removed by purified ether. After treating with charcoal to remove the last traces of picric acid, the solution was concentrated under diminished pressure to about 20 c.c., and excess of pure barium carbonate added. On allowing to remain overnight, the solution was free from sulphation, and only contained *l*-oscine partly present as carbonate. The major portion of the *l*-oscine was readily removed by extraction with freshly purified chloroform, the remainder being retained by the dissolved carbon dioxide. When the latter solution was evaporated to dryness in a vacuum over sulphuric acid and redissolved in a little water, the rest of the oscine was readily extracted by chloroform. In this way, the *l*-oscine was recovered quantitatively as base. The first chloroform extract on complete removal of the solvent crystallised at once. The product was white and amounted to 1.45 grams. It had a specific rotatory power of $[\alpha]_D -52.6^\circ$ in water. It melted at $109-110^\circ$, the same as *dl*-oscine, whilst a mixture of the two showed no depression of the melting point. When recrystallised from light petroleum, it separated in long needles. The melting point was unchanged at $109.5-110.5^\circ$ (corr.).

The specific rotatory power was determined in water:

$$c=1.010; l=2\text{-dcm.}; \alpha=1^\circ 3.6'; [\alpha]_D -52.4^\circ.$$

With Mayer's reagent (potassium mercuric iodide), *l*-oscine base gives no precipitate, but in the form of a salt it gives a crystal-

line precipitate. The presence of a slight excess of acid prevents the separation of crystals. *dl*-Oscine behaves similarly.

Action of Acids and Alkalis on l-Oscine.—A solution of 0.2 gram of *l*-oscine in water having an observed rotation of $\alpha_D -1^{\circ}1'7''$ in a 2-dcm. tube was treated with one drop (0.04 c.c.) of 50 per cent. potassium hydroxide solution. After nineteen hours, the observed rotation was unchanged, $\alpha_D -1^{\circ}1'5''$.

The same solution was heated on the boiling-water bath for an hour. At the end of this period, the rotation was still $-1^{\circ}1'7''$. Five c.c. of 50 per cent. potassium hydroxide were now added, and the solution was boiled for an hour. Making a correction for the change in volume, the observed rotation was unchanged, $\alpha_D -1^{\circ}1'2''$. This means that 0.2 gram of *l*-oscine was not racemised by boiling or an hour with excess of 10 per cent. potassium hydroxide solution.

There was, however, partial racemisation when 0.2 gram of *l*-oscine was heated with 15 c.c. of saturated baryta solution for four hours at 150° , the value of $[\alpha]_D$ having fallen to about one-half its original value.

The action of boiling 10 per cent. hydrobromic acid also failed to racemise *l*-oscine, for 1 gram of *l*-oscine *d*-hydrogen tartrate in 30 c.c. of 10 per cent. hydrobromic acid had an observed rotation, $\alpha_D -21'1''$, in a 2-dcm. tube, and after three hours' boiling the rotation was practically unaltered, $\alpha_D -22'6''$.

d-Oscine Base.—One gram of pure *d*-oscine *d*-hydrogen tartrate was dissolved in 10 c.c. of 5 per cent. sodium hydroxide solution, and the base extracted with purified chloroform. The combined extracts were clarified by shaking with anhydrous potassium carbonate, filtered, and the solvent removed by distillation. The residual base crystallised instantaneously throughout on touching the spot with a glass rod. A similar very high velocity of crystallisation had previously been noticed with the chloroform-free *aceto*-oscine base. It was crystallised from light petroleum, and separated in long, radiating needles, often forming fasciated growths. It melted at $109-110^{\circ}$ ($109.5-110.5^{\circ}$ corr.), and a mixture with pure *dl*-oscine also at the same temperature.

Its specific rotation was determined in water:

$$c = 1.029; l = 2\text{-dcm.}; \alpha_D + 1^{\circ}7'6''; [\alpha]_D + 54.8^{\circ}.$$

d-Oscine Picrate.—The solution of the base which had been used for determining the rotatory power was treated with an equivalent of picric acid (0.3 gram) and rapidly concentrated to about 10 c.c. On allowing to cool, long, radiating, glistening needles of *d*-oscine

picrate (0.3 gram) separated. These melted at $237\text{--}238^\circ$ ($242.5\text{--}243.5^\circ$ corr.). The mother liquors were concentrated, and, when quite cold, the stable dimorph separated in small, flattened rhombs exactly as observed in the case of *l*-oscine picrate. This form also melted at $237\text{--}238^\circ$. A mixture with *d*-oscine picrate, obtained by acid hydrolysis of benzoyl-*d*-oscine, also melted at the same temperature.

d-Oscine Hydrochloride.—To complete the analogy with the *laevo*-series, this salt was prepared and its specific rotation determined. For this purpose, 0.2078 gram of *l*-oscine base was neutralised with the calculated quantity, 13.4 c.c., of *N*/10-hydrochloric acid, and the volume made up to 20 c.c. In a 2-dcm. tube was found α_D $30.1'$, whence $[\alpha]_D$ for the *d*-oscinium ion is $+24.0^\circ$, a value in agreement with $[\alpha]_D - 24.2^\circ$ observed for the *l*-oscinium ion.

The solution just employed was evaporated to dryness and the residue crystallised from absolute alcohol, when *d*-oscine hydrochloride separated in warts with a few isolated prisms. The melting point was $273\text{--}274^\circ$, and the salt was very deliquescent.

Resolution of Benzoyloscine.

This was effected substantially as described by Tutin (T., 1910, 97, 1793).

Five grams of *dl*-oscine hydrobromide were converted into the base, which was heated to 160° with 10 c.c. of benzoyl chloride, when a brisk reaction ensued with simultaneous crystallisation of the benzoyloscine hydrochloride. The solid was collected, washed with ether, and dried at 100° . The crude product melted at 240° and amounted to 5.45 grams, that is, an 83 per cent. yield. It was dissolved in water, and the solution, after decolorisation with a little charcoal, was rendered alkaline with sodium hydrogen carbonate, and completely extracted with chloroform. The benzoyloscine left on removing the chloroform was neutralised to litmus with *d*- α -bromo- π -camphorsulphonic acid, and the salt fractionated from absolute alcohol. The *d*-benzoyloscine bromo-camphorsulphonate was obtained pure after three crystallisations, and melted at $247\text{--}248^\circ$ (Tutin gives $246\text{--}246.5^\circ$). The specific rotation was determined in water:

$$c=1.998; l=2\text{-dcm.}; \alpha_D + 2^\circ 11.3'; [\alpha]_D + 54.74^\circ; [M]_D + 312.3^\circ.$$

The calculated value of the molecular rotatory power of the *d*-benzoyloscinium ion is therefore $312.3\text{--}278.7=33.6^\circ$, whence $[\alpha]_D$ for the *d*-benzoyloscinium ion is $+12.9^\circ$.

Benzoyl-d-oscine Hydrochloride.

Pure benzoyl-*d*-oscine bromocamphorsulphonate (2.8 grams) was triturated with 30 c.c. of water and three molecular proportions of sodium hydrogen carbonate. Benzoyl-*d*-oscine base appeared to separate in needles, which were immediately dissolved by chloroform. The free base, on removal of the solvent, was exactly neutralised with *N*/10-hydrochloric acid, and, after filtering from a little greasy matter, was concentrated rapidly under diminished pressure to a very small volume. On keeping for a short time, the whole of the liquid became filled with perfectly formed rectangular leaflets, which in a few hours were completely transformed into fine needles. These were collected and washed with absolute alcohol. They amounted to 1.1 grams, and melted and decomposed at 280° (287° corr.) (Tutin gives 283—284°). The product was anhydrous. Its specific rotation was determined in dilute aqueous solution:

$c = 2.005$; $l = 2$ -dm.; $\alpha_D = 28.35'$; $[\alpha]_D = 11.79^\circ$; $[M]_D = 34.83^\circ$.

From this is calculated $[\alpha]_D = 13.4^\circ$ for the benzoyl-*d*-oscinium ion, a value which compares favourably with the value $+12.9^\circ$ calculated above from the bromocamphorsulphonate. This value is somewhat higher than Tutin's value, $[\alpha]_D = 10.0^\circ$, which is obtained by calculation from the value $[M]_D = 297.0^\circ$ for benzoyl-*d*-oscine bromocamphorsulphonate.

Hydrolysis of Benzoyl-d-oscine.

With Hydrochloric Acid.—The solution just employed (20 c.c.), containing 0.4001 gram of benzoyl-*d*-oscine hydrochloride, was treated with 9.7 c.c. of 31 per cent. hydrochloric acid, thus bringing the volume approximately to 30 c.c. and the strength of the acid to 10 per cent. The rotation was observed, and the solution was then boiled gently to hydrolyse the benzoyl-*d*-oscine, the rotation being observed at intervals, just as is described under the hydrolysis of *l*-hyoscine (p. 507).

Initial reading. $+20'$; $l = 2$ -dm.

After 1 hour's boiling, $+20.5'$.

After 3 hours' boiling, $+22.0'$.

Hydrolysis was now complete, as there was a copious separation of benzoic acid, and the solution gave no turbidity with Mayer's reagent. The observed rotation is therefore due to the *d*-oscinium ion, and the final value, $+22'$, corresponds with a specific rotation of the *d*-oscinium ion of $+26^\circ$, which is of the same order as that

obtained by calculation from the rotation of *d*-oscine *d*-hydrogen tartrate, namely, $[\alpha]_D^{27.1^\circ}$, and that directly observed, $[\alpha]_D^{24.0^\circ}$, for *d*-oscinium hydrochloride prepared from the tartrate.

The free benzoic acid was removed by extraction with purified ether, and the aqueous liquor concentrated to a syrup under diminished pressure on the water-bath. On dehydration of the syrup by evaporation with absolute alcohol, the residue crystallised. It was dissolved in a little hot absolute alcohol, and, on keeping, 0.07 gram of crystals resembling ammonium chloride were collected. They melted and decomposed in the neighbourhood of 243° (pure *d*-oscine hydrochloride melts at 273°), and were highly deliquescent.

Twenty milligrams of this salt, when treated with an equal weight of picric acid in hot aqueous solution, gave a picrate crystallising in long, fine needles, and later a few rhombs separated, a behaviour which is exactly reproduced by the addition of picric acid solution to the pure *d*- or *l*-oscine *d*-hydrogen tartrates (p. 495). This picrate, when collected and dried, melted and decomposed at 237 – 238° . A mixture with *d*-oscine picrate melted in the same bath at 237 – 238° . The alcoholic mother liquors of the above 0.07 gram of *d*-oscine hydrochloride were combined with picric acid (both in aqueous solution). The addition of the picric acid first precipitated amorphous matter, which was separated, and later a well-crystallised picrate. This salt crystallised in small rhombs, melted and decomposed at 235° , and was in all probability the stable form of *d*-oscine picrate.

With Alkali.—Pure benzoyl-*d*-oscine hydrochloride (0.4009 gram) was dissolved in water, and 5 c.c. of 10 per cent. sodium hydroxide were added. The oily base, which separated rapidly, disappeared on boiling. After an hour, the solution was cooled and neutralised to Congo paper with hydrochloric acid. The precipitated benzoic acid was completely removed by ether extraction, and the extracted aqueous liquor was also free from non-hydrolysed benzoyloscine, as was indicated by the absence of a turbidity on treatment with Mayer's reagent in acid solution. In neutral or very faintly acid solution it gave the well-crystallised precipitate observed with oscine salts. The solution was rapidly concentrated and made up to 20 c.c. In a 2-dcm. tube it gave $\alpha_D + 32.8^\circ$, whence the *d*-oscinium ion has $[\alpha]_D^{25.8^\circ}$, a value in good agreement with that observed by acid hydrolysis, $[\alpha]_D^{26.0^\circ}$, and that observed for pure *d*-oscine hydrochloride, $[\alpha]_D^{24.0^\circ}$.

d-Hyoscine.

The starting material for the isolation of *d*-hyoscine consisted of 75 grams of well-crystallised hydrobromides obtained as a by-product in the manufacture of *l*-hyoscine. It was slightly laevorotatory, having $[\alpha]_D -4.1^\circ$ ($c=2.3$, anhydrous), and contained 9 per cent. of water of crystallisation, which was lost over sulphuric acid. It was regenerated to base, using sodium hydrogen carbonate and chloroform for the purpose, the weight of base being about 55 grams. This was converted into its salt with *d*- α -bromo- π -camphorsulphonic acid, and crystallised from a mixture of dry ethyl acetate and absolute alcohol. In a few days there was a copious, crystalline separation, which was collected, and amounted to 38.5 grams. It was deliquescent and had $[\alpha]_D +46.4^\circ$ ($c=2$), and on two more crystallisations gave 8.8 grams of pure meteloidine bromocamphorsulphonate.

Meteloidine d- α -bromo- π -camphorsulphonate crystallises exceedingly well from absolute alcohol, in which it is soluble to the extent of about 1 part in 10 (boiling), or from a mixture with dry ethyl acetate in clusters of prisms. It also crystallises well from water. It melts at $224-227^\circ$ ($228.5-231.5^\circ$ corr.), and is anhydrous:

0.1410 gave 0.2547 CO_2 and 0.0808 H_2O . $\text{C}=49.3$; $\text{H}=6.4$.

$\text{C}_{13}\text{H}_{21}\text{O}_4\text{N}, \text{C}_{10}\text{H}_{15}\text{O}_4\text{BrS}$ requires $\text{C}=48.75$; $\text{H}=6.4$ per cent.

Its specific rotatory power was determined in water:

$c=2.039$; $l=2\text{-cm.}$; $\alpha_D +1^\circ 56'$; $[\alpha]_D +47.42^\circ$; $[\text{M}]_D +268.7^\circ$.

This value for the molecular rotation is somewhat smaller than that given by Pope and Read for the bromocamphorsulphonic acid ion (T., 1910, 97, 2200). That the meteloidine was inactive was confirmed in two ways:

(1) A small quantity of the above salt was converted into base, avoiding conditions which might favour racemisation by using sodium hydrogen carbonate and chloroform. The base crystallised readily, and was identical in appearance and other properties with a sample of meteloidine kindly supplied by Dr. Pyman, and which was known to be inactive (Pyman and Reynolds, T., 1908, 93, 2077).

(2) One-half a gram of *i*-meteloidine base was converted into its bromocamphorsulphonate, and the solution evaporated to dryness with absolute alcohol. The crystalline residue was triturated with a little dry ethyl acetate, in which the crystals are practically insoluble, and collected. The rotation of this salt, representing

practically the whole of the meteloidine, was found to be the same as the previously described salt:

$$c=1.969; l=2\text{-dcm.}; \alpha+1^{\circ}51'; [\alpha]_D+47.0^{\circ}; [M]_D+266.3^{\circ}.$$

It melted at $224\text{--}225^{\circ}$, and a mixture of the two salts showed no depression of the melting point.

Isolation of d-Hyosicine Bromocamphorsulphonate.—On continuing the fractionation, the original mother liquors gave a second crop of crystals, 24.5 grams, $[\alpha]_D+44.5^{\circ}$, which, after ten recrystallisations, gave 11.6 grams of pure *d*-hyosicine bromocamphorsulphonate melting at $159\text{--}160^{\circ}$ and having $[\alpha]_D+60.1^{\circ}$. This was twice more recrystallised, and gave 8.3 grams with $[\alpha]_D+60.3^{\circ}$.

d-Hyosicine d- α -bromo- π -camphorsulphonate crystallises from a mixture of absolute alcohol and excess of dry ethyl acetate in clusters of glistening, acicular needles. After being dried at 110° it melts at $158\text{--}160^{\circ}$ ($161.5\text{--}163.5^{\circ}$ corr.). Its specific rotation was determined in water at 16° .

$$c=2.005; l=2\text{-dcm.}; \alpha+2^{\circ}25'; [\alpha]_D+60.3^{\circ}; [M]_D+370.5^{\circ}.$$

From this it is calculated that the molecular rotatory power of the *d*-hyoscinium ion is 91.8° and the specific rotatory power $[\alpha]_D$ is $+30.2^{\circ}$ (see *d*-hyosicine hydrobromide). The salt is not deliquescent:

0.2730 lost 0.0022 at 100° . Loss=0.8.

0.1238, dried at 100° , gave 0.2394 CO_2 and 0.0675 H_2O .

C=52.8; H=6.1.

$\text{C}_{17}\text{H}_{21}\text{O}_4\text{N}, \text{C}_{10}\text{H}_{15}\text{O}_4\text{BrS}$ requires C=52.7; H=5.9 per cent.

The fractionation of the various liquors was continued, when further small quantities, 4.5 grams in all, of meteloidine bromocamphorsulphonate, and an additional 12.5 grams of pure *d*-hyosicine bromocamphorsulphonate, $[\alpha]_D+60.5^{\circ}$, were obtained. The original mother liquors now gave 10 grams of a deliquescent salt, $[\alpha]_D+30.8^{\circ}$, and 2.7 grams, $[\alpha]_D+27.3^{\circ}$, both of which had the properties of a slightly impure *l*-hyosicine bromocamphorsulphonate, which requires a calculated value of $[\alpha]_D+29^{\circ}$. On recrystallisation, these gave salts of higher specific rotation. It was not found possible to isolate pure *l*-hyosicine bromocamphorsulphonate from the mother liquors.

d-Hyosicine Hydrobromide.—Six grams of pure *d*-hyosicine bromocamphorsulphonate were converted into base, using chloroform and sodium hydrogen carbonate for the regeneration. The base was neutralised with hydrobromic acid and the solution concentrated under diminished pressure. *d*-Hyosicine hydrobromide separated on keeping in large tablets (2×1 cm.).

d-Hyosine hydrobromide crystallises exceedingly well from water in rectangular-shaped tablets with bevelled edges. It crystallises with three molecules of water, the hydrate melting in a capillary tube at $54.5-55^{\circ}$ ($54.5-55^{\circ}$ corr.). It is rendered anhydrous by drying over sulphuric acid in a vacuum. The behaviour of the anhydrous salt on heating is very varied. It sometimes melts sharply at 168° , resolidifies, and melts at $193-194^{\circ}$ ($197-198^{\circ}$ corr.). Occasionally, the intermediate melting point is not observed at all, or is only indicated by a slight shrinking. If the anhydrous salt is dried for half an hour at 120° , only the higher melting point, $193-194^{\circ}$, is observed. The probable explanation is that the product, which melts at 168° , is either an amorphous form or a metastable, crystalline form of the anhydrous salt, and the transformation of one form into the other is accelerated by rise of temperature. *L-Hyosine hydrobromide* behaves similarly:

0.1842, dried over H_2SO_4 , lost 0.0228. $\text{H}_2\text{O}=12.38$.

0.1813, dried at 100° , lost 0.0226. $\text{H}_2\text{O}=12.47$.

0.1587, " 100° gave 0.0778 AgBr. Br=20.85.

$\text{C}_{17}\text{H}_{21}\text{O}_4\text{N}\cdot\text{HBr}\cdot 3\text{H}_2\text{O}$ requires $\text{H}_2\text{O}=12.33$ per cent.

$\text{C}_{17}\text{H}_{21}\text{O}_4\text{N}\cdot\text{HBr}$ requires Br=20.80 per cent.

The specific rotatory power of the hydrated salt was determined in water:

$c=2.842$; $l=2\text{-cm.}$; $\alpha + 1^{\circ}18.5'$; $[\alpha]_{\text{D}} + 23.02^{\circ}$.

$c=2.525$; $l=2\text{-cm.}$; $\alpha + 1^{\circ}10'$; $[\alpha]_{\text{D}} + 23.10^{\circ}$.

The mean of these values gives for the anhydrous salt $[\alpha]_{\text{D}} + 26.3^{\circ}$ and for the *d*-hyoscinium ion $[\alpha]_{\text{D}} + 33.2^{\circ}$. The latter value is in approximate agreement with that calculated from the molecular rotation of the bromocamphorsulphonate (p. 502), namely, $+30.2^{\circ}$.

d-Hyosine Aurichloride.—*d*-Hyosine bromocamphorsulphonate (0.3 gram) was dissolved in 5 c.c. of warm water, and 5 c.c. of 10 per cent. hydrochloric acid were added, followed by 7 c.c. of gold chloride solution (1 in 30). The aurichloride separated, partly in isolated, minute, rectangular plates, but for the most part in fern-like growths or spangles. It melted at $202-203^{\circ}$ and weighed 0.32 gram. It was twice recrystallised from 2.5 per cent. hydrochloric acid, the melting point each time remaining at $204-205^{\circ}$ ($208-209^{\circ}$ corr.) (decomp.). The recrystallised solid separated in long, flattened, orange-yellow needles with both edges serrated:

0.1266, air-dried, gave 0.0387 Au. Au=30.6.

$\text{C}_{17}\text{H}_{21}\text{O}_4\text{N}\cdot\text{AuCl}_3\cdot\text{HCl}$ requires Au=30.7 per cent.

d-Hyoscine Picrate.—Prepared from *d*-hyoscine bromocamphorsulphonate by double decomposition in aqueous solution, this salt separated as a netted mass of needles melting and decomposing at 187—188° (see *l*-hyoscine picrate).

l-Hyoscine.

l-Hyoscine Hydrobromide.—The properties of this salt are the same as those of *d*-hyoscine hydrobromide. The rotation of the purest hydrobromide crystallised from water was a fraction less than *d*-hyoscine hydrobromide. For various samples, the following values were obtained:

$$\begin{aligned} c &= 2.454; l = 2\text{-dm.}; \alpha = -1.07'; [\alpha]_D - 22.75^\circ. \\ c &= 2.543; l = 2\text{-dm.}; \alpha = -1.09.3'; [\alpha]_D - 22.71^\circ. \\ c &= 2.045; l = 2\text{-dm.}; \alpha = -55.43'; [\alpha]_D - 22.58^\circ. \end{aligned}$$

The mean of the first two values gives $[\alpha]_D - 25.93^\circ$ for the anhydrous salt, and for the *l*-hyoscinium ion $[\alpha]_D - 32.73^\circ$, whereas for the purest *d*-hyoscine hydrobromide the values were 26.3° and 33.2° respectively. The use of *l*- α -bromo- π -camphorsulphonic acid for purifying the *l*-hyoscine would no doubt lead to complete accord between the rotatory powers of the two enantiomorphs.

l-Hyoscine Aurichloride.—*l*-Hyoscine hydrobromide (0.2 gram) was converted into base, using sodium hydrogen carbonate and chloroform. A solution of the hydrochloride was mixed with gold chloride solution, and the *l*-hyoscine aurichloride collected. It weighed 0.28 gram, and melted and decomposed at 204—205°. It was recrystallised from one hundred times its weight of 2.5 per cent. hydrochloric acid, and separated in complex, needle-shaped growths serrated on both edges, exactly as observed for the dextro-enantiomorph. The melting and decomposing point was unchanged (208—209° corr.):

0.1075, air-dried, gave 0.0331 Au. Au = 30.8.

$C_{17}H_{21}O_4N, AuCl_3, HCl$ requires Au = 30.7 per cent.

l-Hyoscine Auribromide.—This was prepared by Jowett's method (T., 1897, 71, 680), by dissolving 0.2 gram of *l*-hyoscine hydrobromide in excess of hydrobromic acid and adding gold chloride solution. The yield was 0.4 gram (m. p. 187—188°). It was recrystallised from boiling 2.5 per cent. hydrobromic acid (40 c.c.), and gave 0.35 gram of long, rectangular, chocolate-red leaflets still melting and decomposing at 187—188° (191—192° corr.):

0.1075, air-dried, gave 0.0258 Au. Au = 24.0.

$C_{17}H_{21}O_4N, AuBr_3, HBr$ requires Au = 24.0 per cent.

l-Hyoscine Picrate.—0.20 Gram of *l*-hyoscine hydrobromide by

double decomposition with a hot saturated picric acid solution gave 0.25 gram of *l*-hyoscine picrate crystallising in slender, primrose-yellow needles (m. p. 187–188°). It required a hundred times its weight of boiling water to dissolve it, and then separated in flat, irregular, six-sided scales covered with striations. Occasionally, these scales were united in the form of long, flat, serrated needles. It now melted and decomposed at 187.5–188.5° (191–192° corr.), and amounted to 0.2 gram.

dl-Hyoscine.

dl-Hyoscine Hydrobromide.—Two and a-half grams each of the purest *d*-hyoscine and *l*-hyoscine hydrobromides were combined and recrystallised from water. The product crystallised exceedingly well with three molecules of water of crystallisation, and was indistinguishable from the active *d*- or *l*-hyoscine hydrobromides. The crystals were collected, and amounted to 3.3 grams. In a capillary tube, the uncrushed crystals melted at 55–58°, but powdered crystals only partly melted up to 60°, owing to rapid loss of water. The anhydrous salt melts at 181–182° (185–186° corr.). The hydrated salt effloresces on exposure to the air, in this respect differing from the active components. A 2.5 per cent. solution in water was optically inactive:

0.2217 uneffloresced salt lost 0.0274 in a vacuum. $H_2O = 12.36$.

0.1943, dried in a vacuum, gave 0.0949 AgBr. $Br = 20.8$.

$C_{17}H_{21}O_4N \cdot HBr \cdot 3H_2O$ requires $H_2O = 12.33$ per cent.

$C_{17}H_{21}O_4N \cdot HBr$ requires $Br = 20.8$ per cent.

dl-Hyoscine Base.—One gram of *dl*-hyoscine hydrobromide was converted into base, using chloroform and sodium hydrogen carbonate. The chloroform-free base was moistened with water, and when kept for some hours in a freezing mixture crystallised in minute needles. The product was collected, washed with water, and, when dried in the air, amounted to 0.55 gram. It melted at 38–40°:

0.1034, in a vacuum over H_2SO_4 , lost 0.0104. $H_2O = 10.1$.

$C_{17}H_{21}O_4N \cdot 2H_2O$ requires $H_2O = 10.6$ per cent.

It was recrystallised by dissolving in a little warm alcohol and adding water until a turbidity developed. On inoculation, it crystallised slowly in well-formed, transparent, chisel-shaped prisms. The melting point was unchanged at 38–40° (38–40° corr.). When dried in a vacuum over sulphuric acid, it lost two molecules of water:

0.0770 lost 0.0082. $H_2O=10.6$.

$C_{17}H_{21}O_4N, 2H_2O$ requires $H_2O=10.6$ per cent.

The anhydrous material consisted of a clear varnish, and had no definite melting point.

The melting point of the dihydrate was unchanged after keeping in a Jena-glass tube for ten months.

dl-Hyoscyne Picrate.—This salt was prepared in aqueous solution by adding a saturated solution of picric acid to a solution of *dl*-hyoscyne hydrobromide. An oil separated at first, but was displaced, on warming, by short needles, which melted and decomposed at $173-174^\circ$. These were recrystallised from one hundred parts of boiling water, and separated in rosettes of long needles, melting and decomposing at $173.5-174.5^\circ$ ($177.5-178.5^\circ$ corr.).

The same salt is obtained from the *dl*-base.

dl-Hyoscyne Aurichloride.—This salt crystallises in long, flat needles with one edge serrated on mixing aqueous solutions of the two components. It melted and decomposed at $214-215^\circ$. On recrystallisation from 2.5 per cent. hydrochloric acid, it separated in stout, boat-shaped crystals melting and decomposing at $218-219^\circ$ (corr.):

0.1175 gave 0.0358 Au. Au=30.5.

$C_{17}H_{21}O_4N, AuCl_3, HCl$ requires Au=30.7 per cent.

dl-Hyoscyne Auribromide.—On mixing *dl*-hyoscyne hydrobromide dissolved in excess of hydrobromic acid with gold chloride solution, this salt crystallises in chocolate-coloured leaflets of indefinite shape melting and decomposing at $209-210^\circ$. On recrystallisation from 50 parts of dilute hydrobromic acid solution, it separated in chocolate-red leaflets very similar in appearance to the *laevo*-salt. The melting and decomposing point was unchanged at $213-214^\circ$ (corr.):

0.1123 gave Au=0.0268. Au=23.9.

$C_{17}H_{21}O_4N, AuBr_3, HBr$ requires Au=24.0 per cent.

Jowett (*loc. cit.*) has described a hyoscyne auribromide melting at 210° , which probably indicates that his starting material, hyoscyne hydrobromide, was optically inactive, or practically so.

Hydrolysis of l-Hyoscyne.

With Hydrobromic Acid.—Pure hydrated *l*-hyoscyne hydrobromide (1.4447 grams), $[\alpha]_D -22.7^\circ$ ($c=2.5$), was dissolved in 30 c.c. of 10 per cent. hydrobromic acid, and the rotation determined. The solution was then boiled gently under reflux, the

rotation being observed at definite intervals by cooling the solution and removing the requisite volume for the observation. On completion of the latter, the solutions were recombined and the boiling started afresh. The following data were obtained, using a 2-dcm. tube:

| | | | |
|----------------------------|-------|------------------------------|-------|
| Initial reading | -141' | After 4 hours' boiling | -159' |
| After 1 hour's boiling ... | -149' | " 6 " " | -161' |
| " 2 hours' " ... | -153' | " 9 " " | -157' |

The solution was now thoroughly extracted with purified ether to remove the *l*-tropic acid. The residual aqueous solution still showed a rotation of $-10'$, and contained non-hydrolysed hyoscine, as it gave a reaction with Mayer's reagent (oscine gives no reaction in acid solution of this strength). The hydrolysis was continued for a further five hours, when the rotation rose to $-11'$, and the reaction for hyoscine was negative. On removal of the *l*-tropic acid by ether, the residual solution was inactive.

The ethereal extracts gave 0.65 gram of crude *l*-tropic acid melting at $125-127^{\circ}$ and having $[\alpha]_D -70.5^{\circ}$ in water ($c=1$). On recrystallisation from water, it melted at $127-128^{\circ}$ and gave $[\alpha]_D -76^{\circ}$ ($c=2$).

The *dl*-oscine hydrobromide solution was concentrated rapidly under diminished pressure to a syrup, when it acquired a purple colour, which disappeared on dilution with water, but in absolute alcohol became brown. The syrupy residue crystallised on inoculating with *dl*-oscine hydrobromide. The crude product melted at 270° and weighed 0.75 gram (theory, 0.78). It was triturated with a little absolute alcohol, and the crystals were collected. The product consisted of granular crystals with a violet colour (probably containing traces of a perbromide (compare Schmidt, *Arch. Pharm.*, 1905, **243**, 567), weighed 0.53 gram, and melted at 280° . A mixture with pure *dl*-oscine hydrobromide (m. p. 282°) also melted at 280° . The filtrate was now evaporated to dryness under diminished pressure, dissolved in 10 per cent. sodium hydroxide solution, and completely extracted with chloroform. On removal of the chloroform, 0.15 gram of base was obtained, which only crystallised on inoculation with the *dl*-oscine base of commerce. It melted at $98-100^{\circ}$, and a mixture with pure oscine melted at 103° .

The products of the hydrolysis are therefore *l*-tropic acid and *dl*-oscine.

With Hydrochloric Acid.—Pure *l*-hyoscine base prepared from 0.5014 gram of *l*-hyoscine hydrobromide, $[\alpha]_D -22.75^{\circ}$ ($c=2.5$), using sodium hydrogen carbonate and chloroform, was dissolved in

30 c.c. of 10 per cent. hydrochloric acid. The rotation was followed as in the case of the hydrobromide.

| | |
|------------------------------|---------------------|
| Initial reading | -52' |
| After 2 hours' boiling | -55'; $l = 2$ -dem. |
| " 4 " " | -56' |
| " 8 " " | -54.5' |

On removal of the *l*-tropic acid (0.15 gram; m. p. 124–125°) by ether, the acid aqueous solution was optically inactive, and when evaporated to dryness with absolute alcohol gave 0.13 gram of *dl*-oscine hydrochloride crystallising in minute, rectangular plates, or associated together in fern-like growths. It was converted into the picrate, which crystallised in small, flattened rhombs or tablets melting and decomposing at 231°. A mixture with pure *dl*-oscine picrate, which crystallises similarly and melts and decomposes at 237–238°, melted intermediately at 232°.

In conclusion, the author desires to express his warmest thanks to Dr. Pyman for his advice and criticism throughout the course of the work.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON, E.C.

[Received, March 26th, 1919.]

XXXVIII.—*The Basic Properties of Oxygen in Organic Acids and Phenols; and the Quadrivalency of Oxygen.*

By JOSEPH KNOX and MARION BROCK RICHARDS.

OXYGEN is usually regarded as a bivalent element in most compounds, but its position in Group VI of the Periodic Table affords good ground for the assumption that it may in certain cases have a higher valency from analogy to sulphur, selenium, and tellurium, all of which may function, not only as bivalent, but also as quadrivalent and sexavalent elements.

The quadrivalency of oxygen has been assumed from time to time to explain the constitution of certain compounds, a summary of the earlier assumptions of this nature being given by Walden (*Ber.*, 1901, **34**, 4185). The work of Collie and Tickle on

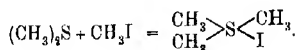
dimethylpyrone (T., 1899, **75**, 710), and of Baeyer and Villiger (*Ber.*, 1901, **34**, 2679; 1902, **35**, 1201), first drew general attention to the subject. The former were of the opinion that only in specially favourable cases could additive compounds containing quadrivalent oxygen be formed, but the latter showed that organic compounds of practically all classes containing oxygen, such as ethers, alcohols, aldehydes, ketones, etc., could combine with acids to give crystalline salts. Since that time, many similar assumptions of the quadrivalency of oxygen have been made, for example, by Bülow and Sicherer for salts of anhydrobenzopyranols and benzopyranols (*Ber.*, 1901, **34**, 3916), by Kehrmann and Mattisson for salts of phenanthraquinone (*Ber.*, 1902, **35**, 343), by Willstätter and Pummerer for compounds of pyrone with acids (*Ber.*, 1904, **37**, 3740), by Farmer for acid salts of monobasic acids (T., 1903, **83**, 1440), by Cohen and Gatecliff for compounds of ethers with nitric acid (P., 1904, **20**, 194; but see also McIntosh, *J. Amer. Chem. Soc.*, 1905, **27**, 1013), by Blaise for compounds of magnesium iodide and zinc iodide with ethers (*Compt. rend.*, 1904, **139**, 1211; 1905, **140**, 661), and by Meyer for salt-like compounds of quinones with acids (*Ber.*, 1908, **41**, 2568).

Much work on this subject has been done by McIntosh and his collaborators, who have prepared additive compounds of ethers, alcohols, aldehydes, ketones, etc., with halogens and anhydrous halogen hydrides (T., 1904, **85**, 919, 1098; 1905, **87**, 784; *J. Amer. Chem. Soc.*, 1905, **27**, 26, 1013; 1906, **28**, 588; 1908, **30**, 1097; 1910, **32**, 542, 1330; 1911, **33**, 70; 1912, **34**, 1273).

Fewer instances have been recorded of the formation of additive compounds of organic acids and phenols with other acids. Baeyer and Villiger obtained no crystalline compounds of acids with acids (*Ber.*, 1901, **34**, 2692). Hoogewerf and van Dorp, however, prepared additive products of sulphuric acid with various organic acids, and of phenols with phosphoric acid (*Rec. trav. chim.*, 1899, **18**, 211; 1902, **21**, 349). Maass and McIntosh obtained a compound of benzoic acid with hydrogen bromide, and of resorcinol with hydrogen bromide and hydrogen chloride (*J. Amer. Chem. Soc.*, 1911, **33**, 70). Pfeiffer also has prepared a number of compounds of organic acids with acids (*Ber.*, 1914, **47**, 1593), and in a recent series of papers Kendall has described the isolation, by the freezing-point method, of additive compounds of organic acids in pairs, of organic acids and phenols with sulphuric acid, and of phenols with organic acids (*J. Amer. Chem. Soc.*, 1914, **36**, 1722, 2498; 1916, **38**, 1309).

It will be seen that the organic compounds which form these

additive products are of the most diverse types. In practically all the cases cited, the organic compound is combined with an acid, forming an unstable additive compound, so that evidently the compound formation is due to basic properties in oxygen of higher valency than two. These additive compounds are generally regarded as "oxonium" compounds, containing quadrivalent oxygen, derived from the hypothetical base $\text{H}_3\text{O}\cdot\text{OH}$, analogous to the sulphonium compounds formed by the passage of sulphur from bivalency to quadrivalency. A typical example is Friedel's dimethyl ether hydrochloride (*Bull. Soc. chim.*, 1875, [ii], **24**, 160): $(\text{CH}_3)_2\text{O} + \text{HCl} = \frac{\text{CH}_3}{\text{CH}_3} > \text{O} < \frac{\text{H}}{\text{Cl}}$ the analogy of which to a sulphonium compound is evident:



The sulphonium salts are derivatives of the strongly basic sulphonium hydroxide, $\text{R}_2\text{S}\cdot\text{OH}$, so that in the salt-like character of the oxonium compounds, and the basic properties of quadrivalent oxygen, there is a parallel in the case of well-known sulphur compounds.

To explain the formation of these additive compounds, special kinds of valencies of oxygen have from time to time been assumed—crypto-valencies, complex valencies, residual affinities. In view of the fact, however, that oxygen may exhibit a higher valency than two in the ordinarily accepted sense, there seems to be no reason to assign special kinds of valencies to oxygen, any more than to sulphur or the other elements of the same group.

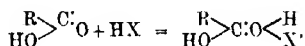
The additive products of organic oxygen compounds with acids have mainly been isolated in the solid state, and very little work has been done on the investigation of these compounds in solution. The compounds are all more or less unstable, and for the most part are decomposed by water into their original constituents. Farmer, for instance, could find no evidence for the existence of acid salts in solution (T., 1903, **83**, 1440), but there is evidence to show that oxonium compounds do exist to a certain extent, at least, in solution. Thus Maass and McIntosh (*J. Amer. Chem. Soc.*, 1913, **35**, 535), by a study of the conductivity measurements of the two component systems—hydrochloric acid and ethyl ether, hydrochloric acid and methyl ether, hydrochloric acid and ethyl alcohol, hydrochloric acid and methyl alcohol—showed the probability of the existence of the compounds in solution. Rørdam (*J. Amer. Chem. Soc.*, 1915, **37**, 557), by comparing the conductivity of a solution

of dimethylpyrone hydrochloride with that of a solution of hydrochloric acid with the same concentration of chlorine ions, electrometrically measured, proved that dimethylpyrone hydrochloride is a real salt showing electrolytic dissociation as well as hydrolytic dissociation into its components. Schuncke (*Zeitsch. physikal. Chem.*, 1894, **14**, 331) found that the solubility of ether is greater in hydrochloric acid solutions than in water, and increases with the concentration of the hydrochloric acid, and Jüttner (*Zeitsch. physikal. Chem.*, 1901, **38**, 56) gave as the reason the formation of ether hydrochloride in solution. Similarly, Sackur (*Ber.*, 1902, **15**, 1242) found that the solubility of cineole increases in hydrochloric, nitric, and acetic acid solutions.

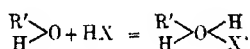
It is possible, therefore, that the existence of other oxonium compounds in solution may be shown by solubility determinations. If additive compounds of organic acids with acids exist in solution, we should expect to find some influence of this salt-formation on the solubility of the organic acid in solutions of the other acids. If no such disturbing influence comes into play, the solubility of the organic acid should continuously diminish with increasing concentration of the solvent acid, in accordance with the law that the solubility of an electrolyte is diminished by the addition of another electrolyte with a common ion.

A few instances have actually been recorded where organic acids do not obey this law. Thus, Herz (*Zeitsch. anorg. Chem.*, 1910, **66**, 93) found that for solutions of oxalic acid in boric acid the solubility increases continuously with the concentration of the boric acid. Stépanov (*Annalen*, 1910, **373**, 221) found that for picric acid in hydrochloric acid solutions the solubility diminishes to a certain point, after which it begins to increase. Masson (*T.*, 1912, **101**, 103) found a similar result for solutions of oxalic acid in hydrochloric and nitric acid solutions.

It seems very probable that these cases may be instances of a general phenomenon, and that the unexpected results obtained for the solubility curves are caused by the existence in solution of an oxonium compound, formed by direct addition of the ions of the solvent acid to an oxygen atom of the organic acid, according to the equation



or, for phenols,



This assumption would be sufficient to account for the observed results. At first with a strong solvent acid, such as hydrochloric or nitric, the effect of the common hydrogen ion prevails, and the solubility diminishes. With increasing concentration of the solvent acid, however, the influence of the formation of the more readily soluble salt becomes stronger, and the solubility reaches a minimum, and finally begins to increase. If the solvent acid is weak, for example, boric acid, the initial decrease may be too small to be measurable; hence the only perceptible effect would be the continuous increase observed by Herz.

If the true explanation of the results observed by Herz, Stépanov, and Masson is the formation of an oxonium compound in solution, we should expect other organic acids to behave in a similar manner, and the present investigation serves to prove that this is actually the case.

EXPERIMENTAL.

I. *Acids.*

The solubilities of a number of organic acids of practically all classes have been determined in solutions of other acids. The number of organic acids which could be used was greatly limited by the lack of suitable methods of analysis. Many of the commonest acids could not be employed, since no sufficiently accurate method is known for their estimation, or since, even at the ordinary temperature, they volatilise from solution on evaporation. Much time was spent in testing various analytical methods given in the literature for a large number of acids, and in determining whether the acids volatilised from solution on evaporation. Amino-acids were avoided, as the presence of the basic amino-group might lead to the formation of salts of the ammonium type. In most cases, the solvent acid is hydrochloric, but experiments have also been performed in nitric, sulphuric, acetic, formic, and lactic acids.

The following series have been investigated:

Monobasic Acids.—Phenylacetic, diphenylacetic, benzilic, *o*-nitrobenzoic, *m*-nitrobenzoic, 3:5-dinitrobenzoic, cinnamic, diphenylene-glycollic, trichlorolactic, mandelic, diphenic, and salicylic acids in hydrochloric acid solutions; trichlorolactic acid in sulphuric acid; mandelic acid in sulphuric, acetic, and formic acids.

Dibasic Acids.—Malonic acid in hydrochloric and sulphuric acids; oxalic acid in sulphuric, acetic, formic, and lactic acids;

phthalic acid in hydrochloric and nitric acids; suberic acid in hydrochloric, nitric, sulphuric, and acetic acids; succinic acid in hydrochloric, nitric, sulphuric, acetic, and formic acids; and tartaric acid in hydrochloric, sulphuric, and acetic acids.

Tribasic Acid.—Citric acid in hydrochloric and sulphuric acids.

Method.—The solubilities were determined at 25°, excess of the solid being shaken for several days in a thermostat with solutions of the solvent acid of varying concentration. After saturation, the clear solution was analysed both for dissolved and solvent acid by one of the following methods:

(1) Solvent acid determined gravimetrically; dissolved acid by direct weighing after evaporation in a vacuum over soda-lime.

This method was used for most of the sparingly soluble acids in hydrochloric acid solutions.

(2) Total acidity determined by titration, with standard sodium hydroxide; dissolved acid by weighing after evaporation either (a) in a vacuum, or (b) on the steam-bath; solvent acid by difference.

This method was used for nitric, acetic, and formic, and in a few cases for hydrochloric, acid solutions.

(3) Total acidity by titration; solvent acid gravimetrically; dissolved acid by difference.

Sulphuric acid solutions were analysed by this method, also cases of acids very readily soluble in hydrochloric acid.

(4) Permanganate methods for oxalic acid solutions: total acidity by alkali; oxalic acid by potassium permanganate, either (a) directly, in sulphuric acid solutions, or (b) after precipitation as calcium oxalate in other cases; solvent acid by difference.

Where an evaporation method was used, a preliminary test was made to ascertain whether the organic acid was left unchanged after evaporation from a solution in the solvent acid.

The results of the various experiments are given in the following tables. The method of analysis is indicated in each case by a number corresponding with the above arrangement, and reference is made to the diagram in which the corresponding solubility curve is to be found. In all cases, the concentrations of the acids are expressed in equivalent normalities.

(1) *Phenylacetic Acid in Hydrochloric Acid. Method 1. Fig. 1.*

| | | | | | | | | | |
|--|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| HCl..... | 0 | 1.417 | 2.890 | 4.313 | 5.770 | 7.175 | 8.590 | 9.988 | 11.36 |
| C ₆ H ₅ O ₂ | 0.1310 | 0.0984 | 0.0833 | 0.0763 | 0.0739 | 0.0756 | 0.0815 | 0.0916 | 0.1099 |

(2) *Diphenylacetic Acid in Hydrochloric Acid. Method 2(b).*

| | | | | | | | | | |
|--|---------|---------|---------|---------|---------|---------|---------|---------|--------------------|
| HCl..... | 0 | 1.620 | 2.913 | 4.512 | 5.973 | 7.349 | 8.889 | 10.27 | 11.74 ¹ |
| C ₁₄ H ₁₂ O ₂ | 0.00060 | 0.00047 | 0.00040 | 0.00036 | 0.00038 | 0.00041 | 0.00042 | 0.00046 | 0.00053 |

(3) *Benzilic Acid in Hydrochloric Acid. Method 2(b).*

| | | | | | | | | | |
|--|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| HCl..... | 0 | 1.537 | 2.977 | 4.440 | 5.934 | 7.356 | 8.803 | 10.25 | 11.69 |
| C ₁₄ H ₁₂ O ₃ | 0.00769 | 0.00332 | 0.00233 | 0.00182 | 0.00172 | 0.00150 | 0.00167 | 0.00195 | 0.00217 |

(4) *o-Nitrobenzoic Acid in Hydrochloric Acid.* Method 1.*

| | | | | | | | | | |
|--|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| HCl..... | 0 | 1.314 | 2.607 | 3.909 | 5.013 | 6.509 | 7.795 | 9.080 | 10.30 |
| C ₇ H ₅ O ₄ N | 0.0470 | 0.0280 | 0.0256 | 0.0239 | 0.0235 | 0.0233 | 0.0237 | 0.0250 | 0.0267 |

(5) *m-Nitrobenzoic Acid in Hydrochloric Acid. Method 1.*

| | | | | | | | | | |
|--|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| HCl..... | 0 | 1.416 | 3.310 | 4.308 | 5.953 | 7.044 | 8.380 | 9.793 | 11.54 |
| C ₇ H ₅ O ₄ N | 0.0214 | 0.0175 | 0.0178 | 0.0183 | 0.0205 | 0.0225 | 0.0256 | 0.0293 | 0.0368 |

* It may be mentioned that Kendall (*Proc. Roy. Soc.*, 1911, [A], 85, 200) gives results for the solubilities of *o*-nitrobenzoic acid, and salicylic acid, in hydrochloric acid solutions; but with the low concentrations of hydrochloric acid used in his experiments, only the decrease in solubility is observed.

| | | | | | | | | | |
|--|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| (6) 3:5-Dinitrobenzoic Acid in Hydrochloric Acid. Method 2(b). | | | | | | | | | |
| HCl..... | 0 | 1.565 | 2.908 | 4.594 | 5.657 | 7.336 | 8.853 | 10.27 | 11.73 |
| C ₇ H ₅ O ₅ N ₂ | 0.00335 | 0.00398 | 0.00470 | 0.00563 | 0.00690 | 0.00841 | 0.00965 | 0.01095 | 0.01240 |
| (7) Cinnamic Acid in Hydrochloric Acid. Method 1. | | | | | | | | | |
| HCl..... | 0 | 2.100 | 4.174 | 6.250 | 8.007 | 10.29 | 10.47 | 10.47 | 10.47 |
| C ₉ H ₈ O ₃ | 0.00385 | 0.00283 | 0.00272 | 0.00318 | 0.00400 | 0.00556 | 0.00572 | 0.00572 | 0.00572 |
| (8) Diphenylglycollic Acid in Hydrochloric Acid. Method 2(b). | | | | | | | | | |
| HCl..... | 0 | 1.952 | 3.907 | 5.843 | 7.745 | 10.29 | 10.47 | 10.47 | 10.47 |
| C ₁₆ H ₁₆ O ₃ | 0.01082 | 0.00492 | 0.00355 | 0.00343 | 0.00352 | 0.00352 | 0.00352 | 0.00352 | 0.00352 |
| (9) Trichlorolactic Acid in Hydrochloric Acid. Method 3. | | | | | | | | | |
| HCl..... | 0 | 1.234 | 2.837 | 4.388 | 5.982 | 7.675 | 8.959 | 10.65 | 12.17 |
| C ₃ H ₅ O ₂ Cl ₃ | 4.024 | 2.545 | 1.425 | 0.984 | 0.760 | 0.659 | 0.624 | 0.57 | 0.60 |
| (10) Trichlorolactic Acid in Sulphuric Acid. Method 3. | | | | | | | | | |
| H ₂ SO ₄ | 0 | 2.525 | 6.166 | 9.588 | 12.75 | 16.28 | 19.38 | 22.28 | 25.34 |
| C ₃ H ₅ O ₂ Cl ₃ | 4.024 | 1.896 | 0.671 | 0.353 | 0.20 | 0.15 | 0.18 | 0.21 | 0.26 |
| (11) Salicylic Acid in Hydrochloric Acid.* Method 1. | | | | | | | | | |
| HCl..... | 0 | 1.459 | 3.057 | 4.374 | 6.104 | 7.311 | 8.730 | 10.20 | 11.54 |
| C ₇ H ₆ O ₃ | 0.01613 | 0.00982 | 0.00715 | 0.00654 | 0.00636 | 0.00666 | 0.00710 | 0.00794 | 0.00856 |

* See footnote on preceding page.

(12) *Diphenic Acid in Hydrochloric Acid. Method 2(b).*

| | | | | | |
|-------------------|---------|---------|---------|---------|---------|
| HCl | 0 | 2.103 | 3.985 | 5.928 | 7.748 |
| $C_6H_5O_4$ | 0.00520 | 0.00182 | 0.00144 | 0.00112 | 0.00118 |

(13) *Mandelic Acid in Hydrochloric Acid. Method 1. Fig. 2.*

| | | | | | | | | | | |
|-------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| HCl | 0 | 1.202 | 2.481 | 3.753 | 5.017 | 6.271 | 7.523 | 8.748 | 9.937 | 10.35 |
| $C_6H_5O_3$ | 1.191 | 0.691 | 0.488 | 0.387 | 0.332 | 0.307 | 0.302 | 0.316 | 0.353 | 0.375 |

(14) *Mandelic Acid in Sulphuric Acid. Method 3. Fig. 2.*

| | | | | | | | | | |
|-------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| H_2SO_4 | 0 | 2.695 | 5.390 | 8.204 | 11.05 | 13.62 | 16.50 | 18.89 | 21.17 |
| $C_6H_5O_3$ | 1.191 | 0.484 | 0.278 | 0.186 | 0.18 | 0.18 | 0.16 | 0.23 | 0.27 |

(15) *Mandelic Acid in Acetic Acid. Method 2(a). Fig. 2.*

| | | | | | | | | | | | | |
|-------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| $C_2H_3O_2$ | 0 | 0.870 | 1.338 | 1.860 | 2.618 | 3.644 | 4.249 | 4.738 | 6.485 | 8.80 | 9.85 | 12.30 |
| $C_6H_5O_3$ | 1.191 | 1.808 | 2.312 | 2.664 | 3.186 | 3.444 | 3.472 | 3.487 | 3.509 | 3.234 | 2.986 | 2.178 |

(16) *Mandelic Acid in Formic Acid. Method 2(a). Fig. 2.*

| | | | | | | | | | |
|-------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| CH_2O_2 | 0 | 2.268 | 4.340 | 6.320 | 8.09 | 10.38 | 12.20 | 13.41 | 13.78 |
| $C_6H_5O_3$ | 1.191 | 1.768 | 2.180 | 2.383 | 2.430 | 2.334 | 2.525 | 2.750 | 3.327 |

(17) *Malonic Acid in Hydrochloric Acid. Method 3. Fig. 3.*

| | | | | | | |
|-------------------|-------|-------|-------|-------|-------|-------|
| HCl | 0 | 4.443 | 6.210 | 8.658 | 10.47 | 11.09 |
| $C_3H_4O_4$ | 15.01 | 7.70 | 5.99 | 4.71 | 4.32 | 4.26 |

| (18) Malonic Acid in Sulphuric Acid. Method 3. Fig. 3. | | | | | | | | | |
|--|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| H_2SO_4 | 0 | 2.727 | 7.030 | 11.76 | 10.05 | 19.92 | 21.84 | | |
| $\text{C}_3\text{H}_4\text{O}_4$ | 13.01 | 11.44 | 6.79 | 4.07 | 3.01 | 3.20 | 4.55 | | |
| (19) Oxalic Acid in Sulphuric Acid. Method 4(a). Fig. 4. | | | | | | | | | |
| H_2SO_4 | 0 | 2.187 | 4.824 | 9.225 | 11.45 | 13.63 | 15.57 | 17.15 | |
| $\text{C}_2\text{H}_2\text{O}_4$ | 2.409 | 1.519 | 1.057 | 0.791 | 0.691 | 0.830 | 1.157 | 1.804 | |
| (20) Oxalic Acid in Lactic Acid. Method 4(b). Fig. 4. | | | | | | | | | |
| $\text{C}_3\text{H}_4\text{O}_4$ | " | 1.337 | 2.718 | 4.051 | 5.357 | 6.477 | 7.647 | 8.709 | 9.52 |
| $\text{C}_2\text{H}_2\text{O}_4$ | 2.409 | 2.228 | 2.054 | 1.856 | 1.633 | 1.412 | 1.171 | 0.938 | 0.832 |
| (21) Oxalic Acid in Formic Acid. Method 4(b). Fig. 4. | | | | | | | | | |
| CH_3CO_2 | 0 | 0.097 | 0.437 | 0.967 | 1.287 | 1.825 | 2.678 | 5.360 | 8.13 |
| $\text{C}_2\text{H}_2\text{O}_4$ | 2.409 | 2.382 | 2.385 | 2.411 | 2.414 | 2.441 | 2.430 | 2.326 | 2.131 |
| | | | | | | | | 1.868 | 1.758 |
| | | | | | | | | 1.496 | 1.568 |
| | | | | | | | | 16.63 | 19.25 |
| | | | | | | | | 12.17 | 21.11 |
| (22) Oxalic Acid in Acetic Acid. Method 4(b). Fig. 4. | | | | | | | | | |
| $\text{C}_2\text{H}_4\text{O}_2$ | 0 | 0.135 | 0.321 | 0.623 | 1.361 | 1.844 | 8.563 | 5.721 | 8.005 |
| $\text{C}_2\text{H}_2\text{O}_4$ | 2.409 | 2.356 | 2.361 | 2.395 | 2.402 | 2.401 | 2.351 | 2.168 | 1.839 |
| | | | | | | | | 1.546 | 1.100 |
| | | | | | | | | 14.03 | 14.21 |
| | | | | | | | | 0.896 | 0.875 |
| | | | | | | | | 12.55 | 0.802 |
| (23) Phthalic Acid in Hydrochloric Acid. Method 1. | | | | | | | | | |
| HCl | 0 | 1.729 | 3.113 | 4.693 | 6.100 | 7.603 | 9.150 | 10.83 | 12.05 |
| $\text{C}_8\text{H}_6\text{O}_4$ | 0.0852 | 0.0422 | 0.0298 | 0.0216 | 0.0172 | 0.0135 | 0.0120 | 0.0128 | 0.0137 |

| (24) <i>Phthalic Acid in Nitric Acid. Method 2(a).</i> | | | | | | | | | |
|---|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| HNO_3 | 0 | 2.977 | 4.077 | 6.718 | 9.027 | 10.40 | 12.60 | 14.42 | 15.99 |
| $\text{C}_6\text{H}_4\text{O}_4$ | 0.0852 | 0.0582 | 0.0470 | 0.0375 | 0.0331 | 0.0325 | 0.0350 | 0.0420 | 0.0577 |
| (25) <i>Suberic Acid in Hydrochloric Acid. Method 1. Fig. 1.</i> | | | | | | | | | |
| HCl | 0 | 1.423 | 2.858 | 4.281 | 5.891 | 7.130 | 8.378 | 9.885 | 11.20 |
| $\text{C}_8\text{H}_{14}\text{O}_4$ | 0.0680 | 0.0498 | 0.0428 | 0.0412 | 0.0432 | 0.0504 | 0.0633 | 0.0805 | 0.1370 |
| (26) <i>Suberic Acid in Nitric Acid. Method 2(a).</i> | | | | | | | | | |
| HNO_3 | 0 | 0.307 | 0.555 | 0.906 | 1.543 | 2.021 | 4.035 | 5.749 | 8.091 |
| $\text{C}_8\text{H}_{14}\text{O}_4$ | 0.0680 | 0.0594 | 0.0580 | 0.0634 | 0.0695 | 0.0839 | 0.1133 | 0.1575 | 0.2231 |
| (27) <i>Suberic Acid in Sulphuric Acid. Method 3.</i> | | | | | | | | | |
| H_2SO_4 | 0 | 1.858 | 5.233 | 7.524 | 11.33 | 18.65 | | | |
| $\text{C}_8\text{H}_{14}\text{O}_4$ | 0.068 | 0.039 | 0.037 | 0.042 | 0.06 | 0.20 | | | |
| (28) <i>Suberic Acid in Acetic Acid. Method 2(a).</i> | | | | | | | | | |
| $\text{C}_2\text{H}_4\text{O}_2$ | 0 | 0.435 | 0.887 | 2.112 | 4.262 | 8.350 | 8.402 | | |
| $\text{C}_8\text{H}_{14}\text{O}_4$ | 0.0680 | 0.0776 | 0.0902 | 0.1340 | 0.2891 | 0.4317 | 0.5846 | | |
| (29) <i>Succinic Acid in Hydrochloric Acid. Method 1. Fig. 5.</i> | | | | | | | | | |
| HCl | 0 | 2.751 | 5.964 | 7.335 | 8.950 | 9.732 | 10.40 | 11.98 | |
| $\text{C}_4\text{H}_4\text{O}_4$ | 1.352 | 0.681 | 0.402 | 0.353 | 0.333 | 0.328 | 0.337 | 0.378 | |

| | | | | | | | | | | | |
|----------|--|---|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| VOL. CXV | HNO ₃ | (30) <i>Succinic Acid in Nitric Acid. Method 2(a). Fig. 5.</i> | | | | | | | | | |
| | | 0 | 1.299 | 3.034 | 5.236 | 6.616 | 8.710 | 11.11 | 13.51 | 15.43 | |
| | C ₄ H ₆ O ₄ | 1.352 | 1.134 | 0.941 | 0.724 | 0.652 | 0.528 | 0.518 | 0.561 | 0.731 | |
| | H ₂ SO ₄ | (31) <i>Succinic Acid in Sulphuric Acid. Method 3. Fig. 5.</i> | | | | | | | | | |
| | | 0 | 1.981 | 3.816 | 4.926 | 8.122 | 10.22 | 13.81 | 17.05 | 20.28 | 23.18 |
| | C ₄ H ₆ O ₄ | 1.352 | 0.908 | 0.683 | 0.563 | 0.388 | 0.34 | 0.30 | 0.30 | 0.39 | 0.69 |
| | C ₂ H ₄ O ₂ | (32) <i>Succinic Acid in Acetic Acid. Method 2(a). Fig. 5.</i> | | | | | | | | | |
| | | 0 | 0.078 | 0.448 | 0.916 | 2.828 | 4.536 | 6.655 | 8.661 | 10.34 | 12.40 |
| | C ₄ H ₆ O ₄ | 1.352 | 1.384 | 1.415 | 1.452 | 1.592 | 1.643 | 1.639 | 1.619 | 1.557 | 1.097 |
| | CH ₃ CO ₂ | (33) <i>Succinic Acid in Formic Acid. Method 2(a). Fig. 5.</i> | | | | | | | | | |
| | | 0 | 0.090 | 0.446 | 0.930 | 3.730 | 5.547 | 7.500 | 11.29 | 15.29 | 17.67 |
| | C ₄ H ₆ O ₄ | 1.352 | 1.369 | 1.397 | 1.408 | 1.501 | 1.531 | 1.449 | 1.228 | 0.944 | 0.796 |
| | HCl | (34) <i>Tartaric Acid in Hydrochloric Acid. Method 3. Fig. 6.</i> | | | | | | | | | |
| | | 0 | 1.257 | 2.568 | 4.466 | 6.303 | 8.144 | 9.890 | 10.51 | 11.17 | 11.17 |
| | C ₄ H ₆ O ₄ | 10.26 | 8.528 | 7.092 | 5.434 | 4.35 | 3.77 | 3.43 | 3.42 | 3.42 | 3.42 |

| | | | | | | | | | |
|--|-------|--------|--------|--------|--------|--------|--------|--------|--------|
| (35) <i>Tartaric Acid in Sulphuric Acid, Method 3, Fig. 6.</i> | | | | | | | | | |
| H_2SO_4 | 0 | 1.798 | 4.043 | 6.807 | 9.895 | 12.54 | 16.46 | 18.10 | 19.85 |
| $\text{C}_4\text{H}_6\text{O}_4$ | 10.26 | 8.51 | 6.64 | 4.73 | 3.18 | 2.43 | 1.93 | 1.77 | 1.86 |
| | | | | | | | | | 22.17 |
| | | | | | | | | | 2.74 |
| (36) <i>Tartaric Acid in Acetic Acid, Method 2(a), Fig. 6.</i> | | | | | | | | | |
| $\text{C}_2\text{H}_4\text{O}_2$ | 0 | 0.23 | 0.60 | 1.23 | 2.63 | 4.24 | 6.12 | 8.30 | 10.89 |
| $\text{C}_4\text{H}_6\text{O}_6$ | 10.26 | 16.69 | 9.875 | 6.515 | 8.717 | 7.718 | 6.548 | 5.151 | 3.505 |
| | | | | | | | | | 14.14 |
| | | | | | | | | | 1.594 |
| | | | | | | | | | 16.92 |
| | | | | | | | | | 9.344 |
| (37) <i>Citric Acid in Hydrochloric Acid, Method 3.</i> | | | | | | | | | |
| HCl | 0 | 0.949 | 2.189 | 3.795 | 5.718 | 7.736 | 9.635 | 10.36 | 11.09 |
| $\text{C}_6\text{H}_8\text{O}_7$ | 12.54 | 11.03 | 9.36 | 7.36 | 5.38 | 4.09 | 3.46 | 3.35 | 3.20 |
| (38) <i>Citric Acid in Sulphuric Acid, Method 3.</i> | | | | | | | | | |
| H_2SO_4 | 0 | 1.089 | 4.206 | 7.145 | 10.83 | 11.46 | 14.24 | 18.18 | 22.37 |
| $\text{C}_6\text{H}_8\text{O}_7$ | 12.54 | 10.57 | 7.97 | 5.61 | 3.28 | 3.07 | 2.23 | 1.76 | 2.88 |
| (39) <i>p-Nitrophenol in Hydrochloric Acid, Method 5(a), Fig. 7.</i> | | | | | | | | | |
| HCl | 0 | 1.630 | 3.277 | 4.993 | 6.552 | 8.106 | 9.817 | 11.29 | 13.33 |
| $\text{C}_6\text{H}_4\text{O}_2\text{N}$ | 0 | 0.1097 | 0.0962 | 0.0613 | 0.0934 | 0.0890 | 0.1093 | 0.1230 | 0.1421 |

(40) *m*-Nitrophenol in Hydrochloric Acid. Method 5(a). Fig. 7.

| | | | | | | | | |
|--|---------|--------|--------|--------|--------|--------|--------|--------|
| HCl | 0 | 1.925 | 3.822 | 5.720 | 7.550 | 9.213 | 10.96 | 11.20 |
| C ₆ H ₅ O ₂ N | 0.0974* | 0.0849 | 0.0834 | 0.0585 | 0.1009 | 0.1130 | 0.1284 | 0.1307 |

(41) Picric Acid in Nitric Acid. Method 6(b).

| | | | | | | | | |
|---|--------|--------|--------|--------|--------|--------|--------|--------|
| HNO ₃ | 0 | 1.022 | 2.059 | 4.161 | 6.289 | 8.334 | 10.47 | 12.47 |
| C ₆ H ₃ O ₇ N ₃ | 0.0578 | 0.0108 | 0.0124 | 0.0237 | 0.0405 | 0.0612 | 0.1006 | 0.1763 |

(42) β -Naphthol in Hydrochloric Acid. Method 5(a).

| | | | | | | | | |
|--|---------|---------|---------|---------|---------|---------|---------|---------|
| HCl | 0 | 1.466 | 2.952 | 4.343 | 5.785 | 7.122 | 8.674 | 11.47 |
| C ₁₀ H ₈ O | 0.00524 | 0.00410 | 0.00360 | 0.00333 | 0.00319 | 0.00316 | 0.00307 | 0.00341 |

(43) Resorcinol in Hydrochloric Acid. Method 5(a).

| | | | | | | | | |
|--|-------|-------|-------|-------|-------|-------|-------|-------|
| HCl | 0 | 0.456 | 1.471 | 3.410 | 4.402 | 6.076 | 7.567 | 9.157 |
| C ₆ H ₆ O ₂ | 0.515 | 5.705 | 4.570 | 3.020 | 2.307 | 1.616 | 1.287 | 1.125 |

* It may be remarked that the value found for the solubility of *m*-nitrophenol in water differs considerably from that given by Vaubel (*J. pr. Chem.*, 1895, [ii], 52, 73), but as no definite particulars are given of the method employed, or of the source of his result, it cannot be regarded as very trustworthy. The compound used in the present case, which was prepared from *m*-nitroaniline, was recrystallised from water, and melted at 96--97°.

(44) *Quinol in Hydrochloric Acid, Method 5(a).*

| | | | | | | | |
|-------------------|-------|-------|-------|-------|-------|-------|-------|
| HCl | 0 | 1.892 | 3.793 | 5.729 | 7.597 | 9.237 | 10.97 |
| $C_6H_6O_2$ | 0.666 | 0.402 | 0.282 | 0.215 | 0.188 | 0.178 | 0.166 |

(45) *Catechol* in Hydrochloric Acid, Method 5(a).*

| | | | | | | | |
|-------------------|------|------|------|------|------|------|-------|
| HCl | 0 | 1.68 | 3.33 | 5.39 | 7.30 | 9.11 | 10.83 |
| $C_6H_6O_2$ | 4.19 | 2.13 | 1.18 | 0.81 | 0.62 | 0.55 | 0.55 |

(46) *Styphnic Acid in Hydrochloric Acid, Method 5(b).*

| | | | | | | | | | |
|----------------------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| HCl | 0 | 1.410 | 2.814 | 4.291 | 5.634 | 6.997 | 8.418 | 11.10 | 11.16 |
| $C_6H_3O_3N_3$ | 0.03179 | 0.00062 | 0.00060 | 0.00072 | 0.00093 | 0.00103 | 0.00197 | 0.00379 | 0.00387 |

(47) *Styphnic Acid in Nitric Acid, Method 6(a).*

| | | | | | | | | | |
|------------------------|---------|----------|----------|----------|----------|----------|---------|---------|---------|
| HNO ₃ | 0 | 1.785 | 4.171 | 6.234 | 8.368 | 10.31 | 11.97 | 13.97 | 15.57 |
| $C_6H_3O_3N_3$ | 0.02179 | 0.001403 | 0.002180 | 0.003274 | 0.005108 | 0.007944 | 0.01298 | 0.02742 | 0.05611 |

(48) *Pyrogallol in Hydrochloric Acid, Method 5(a).*

| | | | | | | | | |
|-------------------|------|------|------|------|------|------|-------|-------|
| HCl | 0 | 1.53 | 3.18 | 5.12 | 6.86 | 8.63 | 10.43 | 10.48 |
| $C_3H_3O_3$ | 4.02 | 2.81 | 1.86 | 1.25 | 1.01 | 0.91 | 0.82 | 0.93 |

* The preliminary test showed that catechol is very slightly volatile at the ordinary temperature in a vacuum, but the regularity of the curve obtained seems to show that in spite of this the results are fairly accurate.

II. *Phenols.*

The solubility of a number of phenols has been determined in the same way, the series investigated being:

Monohydric Phenols.—*p*-Nitrophenol, *m*-nitrophenol, and β -naphthol in hydrochloric acid; trinitrophenol (picric acid) in nitric acid.

Dihydric Phenols.—Resorcinol, quinol, catechol, and trinitroresorcinol (styphnic acid) in hydrochloric acid; trinitroresorcinol in nitric acid.

Trihydric Phenol.—Pyrogallol in hydrochloric acid.

Methods of Analysis.—5. For all phenols in hydrochloric acid, the acid was determined gravimetrically, and the phenol by weighing after evaporation (*a*) in a vacuum, or (*b*) on the steam-bath.

6. For picric acid and styphnic acid in nitric acid, the concentrations of the nitric acid solutions were determined at 25° before adding the solid, owing to the difficulty of titrating solutions containing these phenols. As the phenols are only sparingly soluble, however, any change in volume that might occur when they dissolve could have no appreciable effect on the results. The phenol was determined by weighing, after evaporation (*a*) in a vacuum, or (*b*) on the steam-bath.

Some of the phenols gave deeply coloured solutions, but the residues obtained on evaporation were practically colourless, and a preliminary experiment showed that they were left unchanged when evaporated to dryness with hydrochloric acid or nitric acid.

The results are given in tables 39 to 48, the solubilities of the phenols being given in gram-molecules per litre, whilst the concentrations of the solvent acid are expressed, as before, in equivalent normalities.

Consideration of Results.

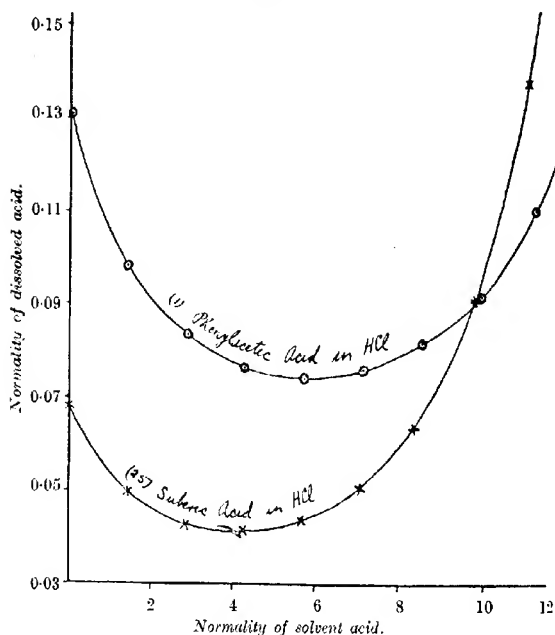
A glance at the solubility curves will suffice to show that the results observed by Herz, Stépanov, and Masson were no isolated phenomena, but that, as regards the solubility of organic acids and phenols in solutions of other acids, deviation from Nernst's law is the rule and not the exception. It will be seen that the curves obtained are of two main types, according as the solvent acid is a mineral or an organic acid, but in each case the assumption of oxonium salt-formation is sufficient to account for the observed results.

Owing to exigencies of space, only a few typical solubility curves can be reproduced. The other solubility curves, which can be

constructed from the tables, will be referred to by the number of the table containing the necessary data. Thus (1) refers to the solubility of phenylacetic acid in hydrochloric acid, and so on.

The curves obtained for solutions in the mineral acids all resemble more or less those obtained by Stépanov and Masson, that is, the solubility diminishes rapidly at first, reaches a minimum, and afterwards increases steadily with increasing concentration of the solvent acid. The results, however, vary somewhat according

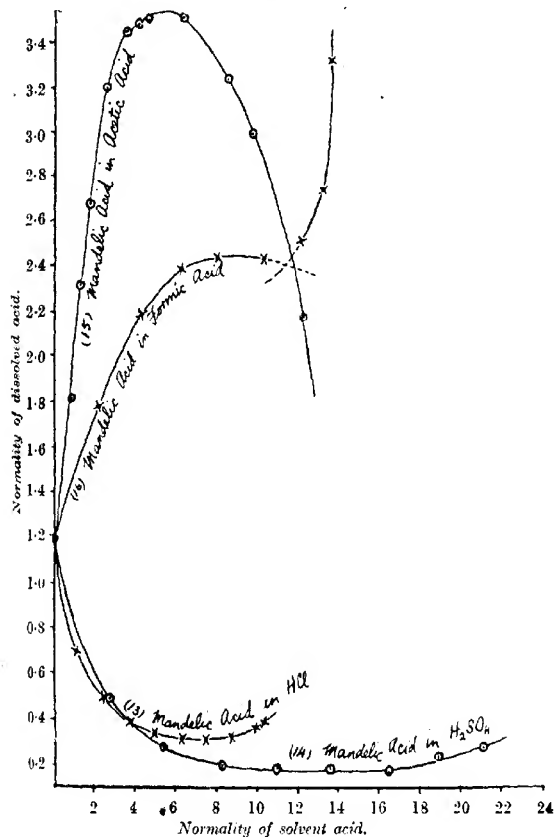
FIG. 1.



to the solubility of the organic acid or phenol, and the concentrations attainable with the mineral acid. Thus with sparingly soluble acids and phenols, such as phenylacetic (1, 25, Fig. 1) and nitrobenzoic acids (4, 5), and the nitrophenols (39, 40, Fig. 7), the curve in every case shows a distinct turning point. Other examples are 2, 3, 6, 7, 8, 11, 12, 23, 24, 25, 26, 27, 39, 40, 41, 42, 46, 47. With very readily soluble substances, such as malonic, citric, and tartaric acids, quinol, and catechol (17, Fig. 3), (34,

Fig. 6), (37, 43, 44, 45, 48), the concentration of hydrochloric acid reached is not sufficient to show clearly the upward tendency of the curve, although the general shape makes it evident that the

FIG. 2.

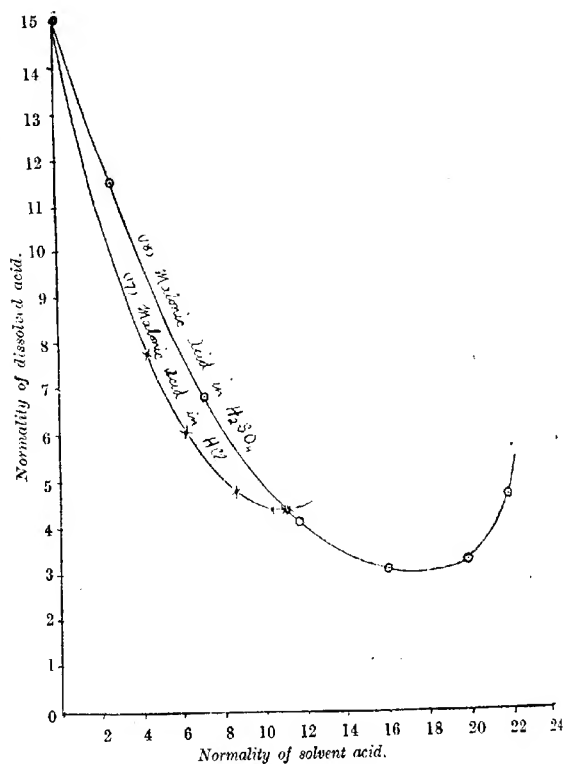


ve has reached its minimum at the concentration attained, and just about to turn upwards—a conclusion which is further stified by the fact that in sulphuric acid solutions, where the concentrations attainable are considerably greater, even the very

readily soluble acids give a definite turning point (18, Fig. 3). (35, Fig. 6), (38).

When the solvent acid is organic, modification of the shape of the curve results from two causes, namely, (a) the weakness of organic acids in general, and (b) the wide difference between the

FIG. 3.



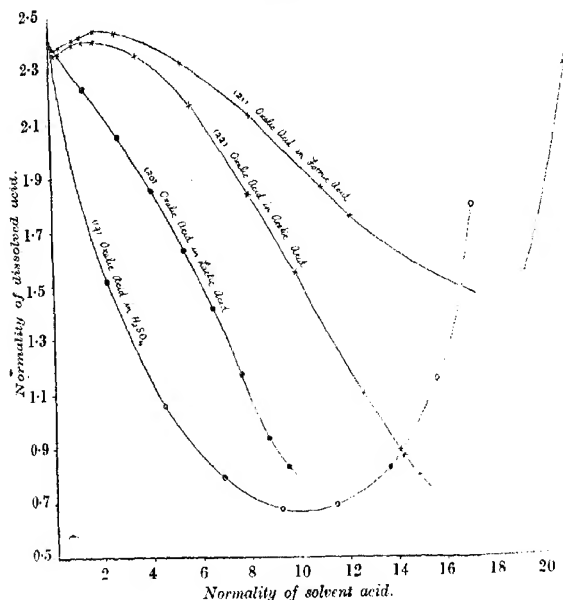
solubilities of the dissolved acid in water and in the organic acid solvent.

(a) When both solvent and dissolved acids are weak, the effect of the common hydrogen ion is, as a rule, too small to be measured. Of the acids the solubilities of which were determined in an organic acid solution, oxalic acid is the only one of sufficient acidic strength

to show any perceptible initial decrease in solubility (21, 22, Fig. 4). The others show increase in solubility from the beginning, except tartaric in acetic (36, Fig. 6), and oxalic in lactic acid (20, Fig. 4), where no evidence of salt-formation was obtained.

(b) If the dissolved acid is more readily soluble in the solvent organic acid than in water, the resulting curve shows a continuous increase—an increase which may be partly due to salt-formation or entirely due to increasing solubility in the solvent acid, so that

FIG. 4.

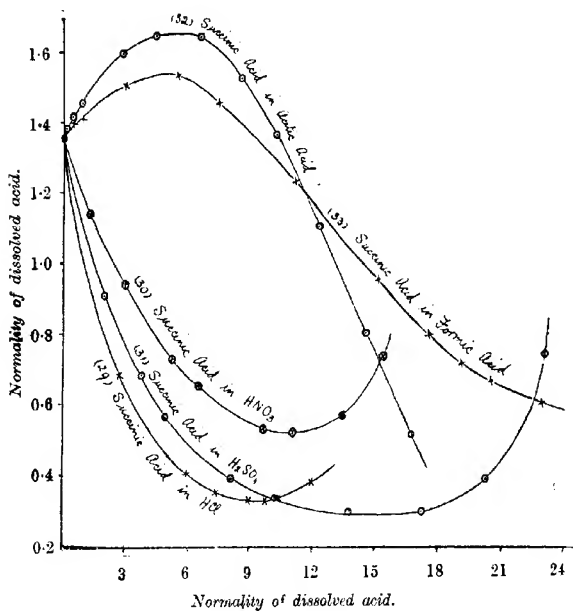


no conclusion as to salt-formation can be drawn. An instance of this may be seen in the curve for suberic acid in acetic acid (28). Other cases give clear evidence of salt-formation, the curve showing an initial increase in solubility, owing to the formation of the more readily soluble salt, with a subsequent decrease, caused by decreasing solubility in the solvent acid. The curves which show this effect clearly are: (1) succinic acid in acetic and formic acids (32, 33, Fig. 5), (2) oxalic acid in acetic and formic acids (here the ionic effect is first perceptible, before the increase due to salt-

formation) (21, 22, Fig. 4), and (3) mandelic acid in acetic and formic acids (15, 16, Fig. 2).

(It will be observed that in three of these cases, namely, oxalic acid in acetic and formic acid solutions, and mandelic acid in formic acid, there is apparently a break in the curve. The cause of this has not been investigated, but Masson, who obtained a similar break for oxalic acid in nitric acid, attributed the result to dehydration of the oxalic acid.)

FIG. 5.

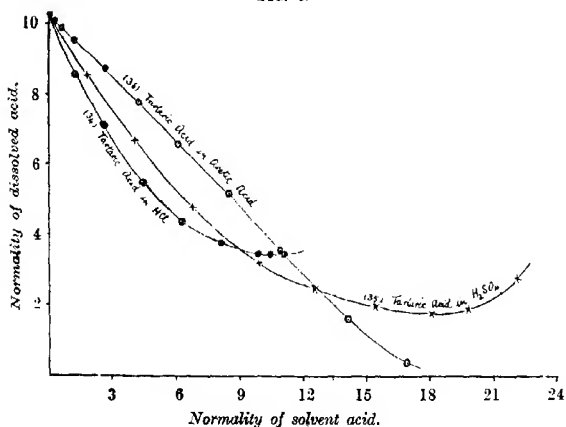


From the curves, it may be inferred that salt-formation does not take place with equal readiness in all the mineral acids. Where curves have been determined for the same organic acid or phenol both in hydrochloric and nitric acid solutions, it will be seen that in each case the nitric acid curve lies above that for hydrochloric acid, evidently indicating that additive compounds are formed more readily with nitric acid; see, for example, the curves for succinic (29, 30, Fig. 5), phthalic (23, 24), suberic (25, 26), and

styphnic acids (46, 47) in hydrochloric and nitric acid respectively.

Again, a comparison of the curves for the same acid in hydrochloric and sulphuric acid solutions shows uniformity of behaviour in all the cases investigated. There is at first a more rapid decrease in solubility in hydrochloric than in sulphuric acid (probably due to the greater acidic strength of hydrochloric acid, and the correspondingly greater ionic effect), but the turning point is more quickly reached and the hydrochloric acid curve soon cuts the other, from which we may infer that salt-formation takes place with greater ease in hydrochloric acid. A comparison of the curves for succinic (29, 31, Fig. 5), citric (37, 38), tartaric (34, 35, Fig. 6),

FIG. 6.

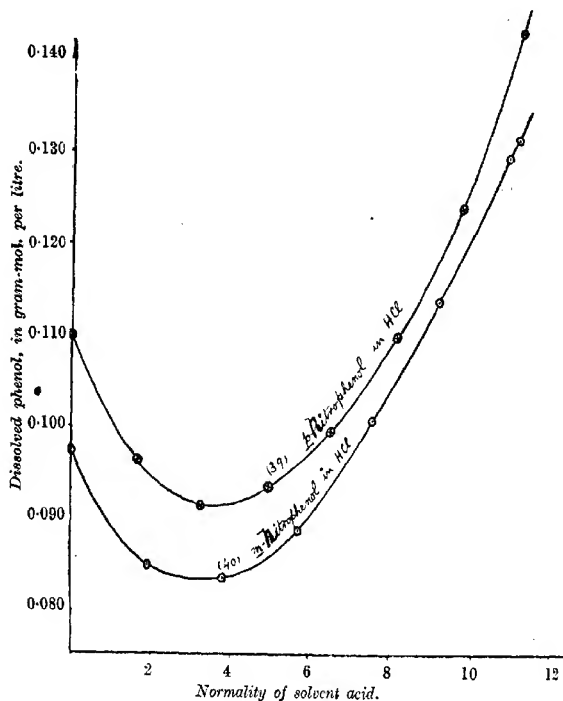


malonic (17, 18, Fig. 3), mandelic (13, 14, Fig. 2), and trichlorolactic acids (9, 10) in hydrochloric and sulphuric acids, respectively, will make this clear. (In the case of suberic acid [25, 27], the result appears to be similar, but owing to the small solubility of suberic acid, and the necessity for estimating the suberic acid in sulphuric acid solutions by difference, this curve is not sufficiently accurate to enable the distinction between the two curves to be clearly seen.) It would therefore appear that, of the mineral acids, sulphuric acid shows the least tendency to salt-formation, whilst nitric acid shows the greatest.

No quantitative connexion can be established between the turning point of the curve and the strength of the organic acid in

question. Kendall found that, in general, for additive compounds, both of organic acids in pairs and of organic acids with sulphuric acid, the tendency towards the formation of additive compounds is dependent on the difference in acidic strengths. Very weak organic acids most readily form additive compounds, and an

FIG. 7.



increase in the acidic strength is accompanied by a diminution or loss of this property. The rule is, however, merely qualitative. This result is, in general, confirmed by the present investigation, although the question is complicated by the fact that the turning point in the solubility curve depends largely on the solubility of the organic acid.

General Summary of Results.

From determinations of the solubility of organic acids and phenols in solutions of other acids, it has been shown that in such solutions compounds are formed between the organic acid or phenol and the solvent acid. The most probable explanation is that the organic acids and phenols contain a basic oxygen atom, and that this forms salts of the oxonium type with the solvent acid, the oxygen becoming quadrivalent. This view is strongly supported by the work of Kendall, whose earlier papers were published during the progress of the present research.*

Thanks are due to the Carnegie Trust for a Fellowship that has enabled one of the authors to take part in this investigation.

CHEMICAL DEPARTMENT,

UNIVERSITY OF ABERDEEN.

[Received, February 8th, 1919.]

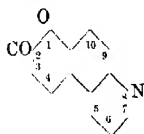
XXXIX.— ψ -1 : 8-isoNaphthoxazones.

By BIMAN BIHARI DEY and MAHENDRA NATH GOSWAMI.

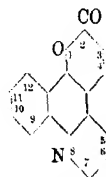
By the fusion of a pyridine with a benzene nucleus, the condensed quinoline ring is formed, and in a similar manner it is conceivable that the coumarin ring would give rise to a class of derivatives which might be represented as ψ - β -naphthoxazones,† their relation-

* Kendall has since published other papers on the same subject, reference to which will be found in the concluding paper of the series (*J. Amer. Chem. Soc.*, 1917, **39**, 2303), in which he sums up the results of his investigations. The above research was completed early in 1916, but for various reasons publication of the results has been delayed.

† As the compounds described in this paper do not contain the true oxazine ring, they are regarded as being derived from ψ -naphthoxazines, thus :

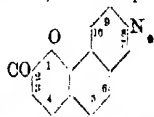


ψ -1 : 8-isoNaphthoxazone.

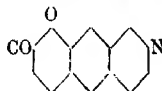


ψ -Benzo-1 : 8-isonaphthoxazone.

Isomerides of ψ -1 : 8-isonaphthoxazone will thus receive the name :

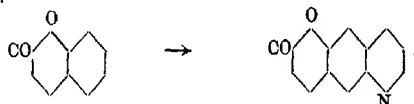


ψ -1 : 8- α -Naphthoxazone.

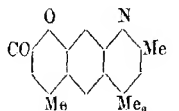


ψ -1 : 8- β -Naphthoxazone.

ship to coumarins being analogous to that of quinoline to benzene:



Substances of the latter class, so far as it has been possible to ascertain, are practically unknown, only one instance being encountered in the literature where a compound probably belonging to this category has been mentioned (Pechmann and Schwarz, *Ber.*, 1899, **32**, 3701). This substance was obtained as a by-product in the condensation of *m*-aminophenol and ethyl acetoacetate, where, in addition to the expected 7-amino-4-methylcoumarin, a small amount of a solid (m. p. 268°) was isolated, which was regarded as a dihydroquinocoumarin, and assigned the following structure:



The evidence adduced in favour of its constitution is not complete, and no further work appears to have been carried out on the subject.

The reactions which are of general applicability in the synthesis of quinoline and its allies, namely, the Skraup, the Doebner-Miller, and the Knorr reactions, are all based on the condensations of aniline or other primary aromatic amines; the same methods, with slight modifications, have now been applied to the synthesis of the ψ -naphthoxazones from the aminocoumarins and the aminonaphthacoumarins, in which the amino-groups are attached to the benzene nucleus. These compounds have been shown by previous investigators to resemble the aromatic amines in their chemical behaviour, and they may readily be diazotised and reduced to the corresponding coumarylhydrazines, etc. (Morgan and Micklethwait, *T.*, 1904, **85**, 1233; Clayton, *P.*, 1911, **27**, 246).

These considerations led to the present investigation, a systematic study of this new class of substances being also considered desirable in view of certain questions that arose with regard to the connexion between their structure and physiological properties.

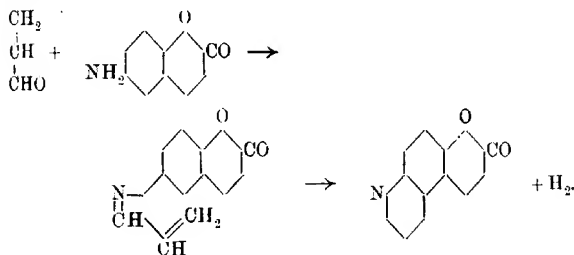
The present communication deals with the application of the Skraup synthesis to the preparation of the ψ -naphthoxazones, the

results obtained with the other reactions being incomplete and reserved for a future communication.

The Skraup reaction, which depends on the condensation of aromatic amines with glycerol and sulphuric acid in the presence of an oxidising agent, is apt to be rather violent when applied to the aminocoumarins, and it was found that the success of the operation depended to a great extent on the careful regulation of the temperature at the commencement of the reaction. It was also observed that, instead of using a mixture of nitro- and aminocoumarins, as is generally done in these reactions, the nitro-coumarins could be employed alone, without diminishing the yield of the ψ -naphthoxazones to any appreciable extent.

This observation greatly simplified the process of this synthesis, as the aminocoumarins were sometimes rather difficult to prepare from the corresponding nitro-compounds.

On treating 6-nitrocoumarin with allyl alcohol, it was reduced to the amino-compound (compare Brunner and Chuard, *Ber.*, 1885, 18, 447), and it may therefore be legitimately assumed that allyl alcohol is formed in one of the stages in the condensation and is then oxidised to the corresponding aldehyde by the nitro-compound, which is reduced in the process. The amino-compound now serves to combine with the acetaldehyde, after which the reaction takes the usual course:



In their chemical characteristics, the ψ -naphthoxazones do not differ materially from the quinolines, except in their behaviour towards hot alkali hydroxides, which dissolve these substances with a deep colour. This is evidently due to the hydrolysis of the pyrone ring, and the solution presumably contains an unstable acid; on carefully neutralising the alkaline solution in the cold, the original substance is slowly deposited in the crystalline state.

The ψ -naphthoxazones, as tertiary bases, readily form salts, a large variety of the double salts having been prepared in the course of this investigation; amongst these, the dichromates, the

ferrocyanides, and the double potassium mercuri-iodides are very characteristic, and form crystals having a definite structure. They also give characteristic precipitates with the general alkaloidal reagents: Wagner's solution gives a deep orange-brown, crystalline precipitate of the iodide, Scheibler's reagent gives a white, crystalline precipitate of the phosphotungstates, and Sonnenschein's reagent gives a curdy precipitate of the corresponding phosphomolybdate.

Like the tertiary amines, they also unite with alkyl haloids in molecular proportions. A feature of some interest which has arisen from a study of these *N*-alkyl iodides is the remarkable phenomenon of colour exhibited by members of the series in the solid state and in solution. Although the ψ -naphthoxazones are generally colourless, and form colourless solutions in dilute mineral acids, their additive products with the alkyl iodides possess a deep colour varying in shade from dark yellow to scarlet-red. The aqueous solutions of these iodides, however, which are strongly ionised, are practically colourless.

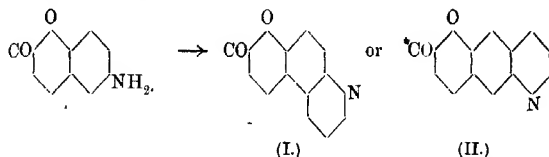
In seeking an explanation for this behaviour, the influence of ionisation, and also, perhaps, that of the alkyl group and the halogen, has to be taken into account, and it seems feasible, therefore, to suggest that the ions, basic and acidic, are colourless, whilst the undissociated molecule of the *N*-alkyl iodide is intensely coloured.

If, moreover, this interpretation is correct, it would be reasonable to expect that the solutions of these iodides in non-ionising media would be coloured. This has been observed to be the case, for although the ordinary non-ionising solvents, like benzene, chloroform, etc., were found to have little or no solvent action on these iodides, the latter dissolved in warm toluene or xylene, the solutions being generally purple with an intense pink fluorescence.

In the reduction of the ψ -naphthoxazones, the pyridine ring is first hydrogenised. The *N*-tetrahydro- ψ -naphthoxazones crystallise in golden-yellow needles, and their chemical behaviour coincides exactly with that of the fatty, aromatic secondary amines; the presence of the imino-group in their molecules is shown by the characteristic nitroso- and acyl derivatives which they form with nitrous acid, acetic anhydride, etc.

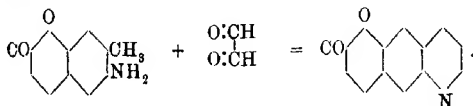
The problem of ascertaining the constitution of the ψ -naphthoxazones has been greatly simplified by a consideration of the nature of the reactions employed in their synthesis. The occurrence of the pyridine ring in the molecule has been placed beyond doubt by the isolation of quinoline by the distillation of the unsubstituted ψ -naphthoxazone with zinc dust. The next question

of importance that has to be settled in order to arrive at a definite structure for each individual member of the series concerns the manner of attachment of the pyridine to the benzene nucleus. Thus, the reaction by which ψ -1:8-naphthoxazone is synthesised from 6-aminocoumarin may follow two different courses, according as the carbon atom adjacent to the amino-group taking part in the condensation occupies position 5 or 7 in the benzene ring. The compound in question may therefore be assigned either of the two following structures:



Although any direct evidence which might enable a decision to be made between these two possible constitutions is still lacking, the formula I appears to be the more plausible, and is also in harmony with certain general observations regarding the process of this condensation. Thus the substitution of a methyl group in position 7 does not hinder the progress of this reaction to the slightest extent, and this behaviour would be difficult to explain if it were assumed that the pyridine ring attached itself in the first place to the 7-carbon atom. The synthesis of alizarin-blue is another example of a similar nature where the condensation takes place smoothly with the *peri*-carbon atom corresponding with the 5-position in the coumarin ring.

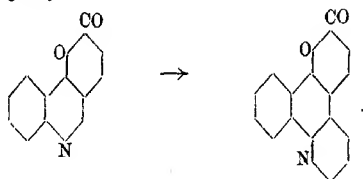
The best solution of the problem appeared to lie in the synthesis of a ψ -naphthoxazone of structure II from 6-amino-7-methylcoumarin and glyoxal, which, in the presence of alkalis, were expected to condense in the following manner (compare Kulisch, *Monatsh.*, 1895, 15, 277):



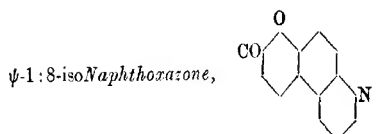
Attempts in this direction, however, have hitherto been unfruitful, and further experiments are in progress.

The determination of the structures of the ψ -benzoisonaphthoxazones which have been obtained by analogous reactions from 6-nitro- and 6-amino-1:2- α -naphthapyrones does not present much difficulty, as in these cases only the carbon atom 5 is free to

participate in the reaction, which can therefore proceed only in the following way:



EXPERIMENTAL.



This substance was first prepared from 6-aminocoumarin by heating it with glycerol and sulphuric acid in the presence of 6-nitrocoumarin as the oxidising agent, according to the original directions of Skraup (*Monatsh.*, 1880, **1**, 316). The use of aminocoumarin was dispensed with later and the nitro-compound employed alone, the following conditions being found to give the most satisfactory results.

6-Nitrocoumarin (16 grams) and glycerol (19 c.c.) were mixed together, and concentrated sulphuric acid (17 grams) was gradually added, the mixture being cautiously heated in an oil-bath. A violent reaction set in at $145\text{--}150^\circ$, and as soon as this occurred the flask was removed from the bath and shaken vigorously. After the first reaction had subsided, the contents, which had now assumed a dark, tarry appearance, were again gradually heated to $160\text{--}170^\circ$, and maintained at this temperature for five to six hours. After cooling, the solid mass was broken up and repeatedly warmed with small amounts of water, and filtered until the filtrate ceased to exhibit a blue fluorescence. The latter, on keeping, deposited a small amount of crystals, which were found to be unchanged nitrocoumarin. This was removed and the acid filtrate rendered alkaline with dilute sodium hydroxide, care being taken to avoid an excess, as the freshly precipitated ψ -1:8-isonaphthoxazone dissolves to a considerable extent in dilute alkali hydroxide even in the cold. The voluminous, pale yellow precipitate was collected, washed with cold water, and crystallised twice from boiling dilute alcohol with the aid of animal charcoal.

Thin, silky needles were deposited having a faint yellow colour and melting at 232° (uncorr.). The yield of the crystallised substance amounted to a little more than 6 grams, approximating to 40 per cent. of that required by theory:

0.0930 gave 0.2488 CO_2 and 0.0326 H_2O . $\text{C}=72.9$; $\text{H}=3.9$.

0.1333 „ 8.3 c.c. N_2 at 30° and 745 mm. $\text{N}=6.9$.

$\text{C}_{12}\text{H}_7\text{O}_2\text{N}$ requires $\text{C}=73.1$; $\text{H}=3.5$; $\text{N}=7.1$ per cent.

The substance dissolves readily in alcohol, ether, chloroform, etc., to form colourless solutions, but its solutions in dilute sulphuric and hydrochloric acids exhibit a pale blue fluorescence, which is best seen on dilution. The crystallised substance is insoluble in dilute sodium hydroxide solution in the cold, but dissolves on boiling to give a deep yellow solution. The latter, on cooling and carefully neutralising with dilute sulphuric acid, slowly deposits the original material in a crystalline condition.

The *hydrochloride* is precipitated on passing dry hydrogen chloride into a solution of the substance in 90 per cent. alcohol. It forms a white, granular powder after being washed with absolute alcohol.

The *mercurichloride* crystallises from water in long, colourless, soft needles.

The *potassium mercuri-iodide*, which is first obtained as a curdy, white precipitate on adding Meyer's solution, very quickly changes into lustrous, leafy crystals.

The *picrate* is precipitated on mixing the constituents in hot benzene solution. It forms a yellow, crystalline powder melting at 212° .

The *platinichloride*, prepared by the usual method, crystallises in yellowish-brown needles:

0.0757 gave 0.0177 Pt. $\text{Pt}=23.4$.

$(\text{C}_{12}\text{H}_7\text{O}_2\text{N})_2, \text{H}_2\text{PtCl}_6, \text{H}_2\text{O}$ requires $\text{Pt}=23.6$ per cent.

The *aurichloride* forms a bright yellow, crystalline precipitate, which rapidly turns brown in the air.

The *dichromate* crystallises in orange-red prisms, which are almost insoluble in water.

The *ferrocyanide* forms a shining, crystalline powder, which has a very characteristic colour resembling that of catechu. It dissolves in boiling water, the solution having an intense blue fluorescence. The ferrocyanide appears to be partly decomposed in the process of boiling its solution, as, on cooling the aqueous solution, the salt does not crystallise out, but a deep blue powder is gradually deposited along with clusters of small, colourless needles, which were identified as those of the original base.

A series of ammonium iodides has been obtained from ψ -1:8-isonaphthoxazone by union with the alkyl iodides. These were prepared by the general method of heating the base with the alkyl iodide, with the addition of a little absolute alcohol, at 140° in sealed tubes. They possess a dark yellow to red colour, are fairly readily soluble in water, and crystallise on concentrating their aqueous solutions. The following have been prepared:

ψ -1:8-isonaphthoxazone N-methiodide crystallises in thin, scarlet-red plates melting at 246° . The aqueous solution has a faint yellow colour:

0.1655 gave 0.1138 AgI. $I = 37.15$.

$C_{13}H_{10}O_2NI$ requires $I = 37.46$ per cent.

It is practically insoluble in the ordinary organic solvents, such as benzene, ether, chloroform, etc., but readily dissolves in warm xylene to form a dark red solution with a fine violet fluorescence.

The N-ethiodide, $C_{14}H_{12}O_2NI$, forms orange-red crystals melting at 206° . Its solution in xylene has a reddish-violet colour and exhibits an intense pink fluorescence.

The N-n-butyl iodide, $C_{18}H_{16}O_2NI$, forms a dark yellow powder melting and decomposing at 209° . It agrees with the foregoing derivatives in its general behaviour.

The N-amyl iodide, $C_{17}H_{18}O_2NI$, melts and decomposes at 210° . It closely resembles the butyl derivative in its physical properties.

In order to examine the effect of the displacement of the alkyl groups by other complex groups on the colour of these substances, the following compounds were prepared, the first two of which were practically colourless, whilst the last had a pale yellow tint.

The N-allyl bromide, $C_{15}H_{12}O_2NBr$, forms small, white needles melting and decomposing at 320° .

The N-benzyl chloride, $C_{19}H_{14}O_2NCl$, crystallises from water in green needles melting at 265° .

The N-phenylacetyl bromide, $C_{20}H_{14}O_2NBr$, forms a pale yellow, crystalline powder melting and decomposing at 350° .

5:6:7:8-Tetrahydro- ψ -1:8-isonaphthoxazone.

ψ -1:8-isonaphthoxazone (2 grams) was dissolved in concentrated hydrochloric acid (30 c.c.), granulated tin (5 grams) added, and the mixture gently boiled on a sand-bath under reflux for seven to eight hours. Next day water was added, and the tin was removed as sulphide. The filtrate was concentrated to about 100 c.c., and rendered alkaline with dilute ammonia; on cooling, the tetrahydro-derivative slowly separated in golden-yellow needles.

A single crystallisation from hot water, in which it was moderately soluble, rendered it quite pure, and the substance then melted sharply at 148°:

0.1624 gave 0.4257 CO₂ and 0.0818 H₂O. C=71.5; H=5.61.

0.1884 „ 12.2 c.c. N₂ at 26° and 742 mm. N=7.3.

C₁₂H₁₁O₂N requires C=71.64; H=5.47; N=7.00 per cent.

The N-nitroso-derivative, prepared in the usual manner, crystallised from alcohol in almost colourless needles melting at 175°:

0.1448 gave 15.15 c.c. N₂ at 22° and 757 mm. N=12.1.

C₁₂H₁₀O₃N₂ requires N=12.17 per cent.

The benzoyl derivative, C₁₉H₁₃O₃N, forms colourless plates, sparingly soluble in alcohol and melting at 252°.

9-Methyl- ψ -1:8-isonaphthoxazone was prepared from 6-nitro-7-methylcoumarin, the same precautions being taken as in the case of the preparation of the unsubstituted naphthoxazone. The product amounted to 3 grams from 8 grams of the nitro-derivative, the yield being approximately 35 per cent. of the theoretical. It crystallises in colourless needles melting at 200°:

0.1040 gave 6.4 c.c. N₂ at 30° and 744 mm. N=6.8.

C₁₃H₉O₂N requires N=6.63 per cent.

The picrate crystallises in prismatic needles melting at 209°.

The dichromate crystallises from water in orange-yellow, flat prisms.

The ferrocyanide forms a chocolate-red, crystalline powder.

The platinumchloride crystallises in deep yellow, small needles.

The aurichloride forms an amorphous, yellow precipitate.

The mercurichloride crystallises in soft, colourless, woolly needles.

The potassium mercuri-iodide forms clusters of pale yellow, prismatic needles.

5:6:7:8-Tetrahydro-9-methyl- ψ -1:8-isonaphthoxazone, prepared from the corresponding methylnaphthoxazone by reduction with tin and hydrochloric acid, crystallises in golden-yellow needles melting at 180°:

0.1650 gave 9.9 c.c. N₂ at 27° and 751 mm. N=6.75.

C₁₃H₁₃O₂N requires N=6.51 per cent.

The nitroso-derivative, C₁₃H₁₂O₃N₂, forms a colourless, crystalline powder melting at 155°.

4:9-Dimethyl- ψ -1:8-isonaphthoxazone was obtained in a 20 per cent. yield by heating 6-nitro-4:7-dimethylcoumarin (m. p. 250°) with glycerol and sulphuric acid under the usual conditions. It crystallises from warm alcohol in silky needles melting at 238°:

0.1249 gave 7 c.c. N_2 at 27° and 748 mm. $N=6.3$.

$C_{14}H_{13}O_2N$ requires $N=6.20$ per cent.

The *picrate* crystallises in yellow needles melting at 197° .

The *dichromate* forms a dark red, crystalline powder.

The *ferrocyanide* forms intense red, small prisms decomposing above 300° .

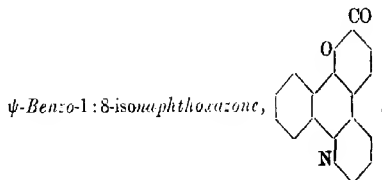
The *methiodide*, $C_{15}H_{14}O_2NI$, crystallises from water in dark brown needles melting at 195° .

5 : 6 : 7 : 8-Tetrahydro-4 : 9-dimethyl- ψ -1 : 8-isonaphthoxazone crystallises from alcohol in bright yellow needles melting at 190° . It is practically insoluble in hot water:

0.1438 gave 7.8 c.c. N_2 at 26° and 748 mm. $N=6.15$.

$C_{14}H_{13}O_2N$ requires $N=6.10$ per cent.

The *nitroso*-derivative, $C_{14}H_{14}O_3N_2$, prepared by adding a very dilute solution of sodium nitrite to a solution of the base in dilute hydrochloric acid at 0° , forms a colourless powder melting at 161° .



The starting point in the synthesis of this substance is 6-nitro-1:2- α -naphthapyrone, $C_{13}H_7O_4N$, which does not appear to have been described before. It was prepared by the ordinary process of nitrating 1:2- α -naphthapyrone dissolved in glacial acetic acid, adding concentrated sulphuric acid, and warming the mixture on the water-bath. It separates from hot glacial acetic acid in pale yellow nodules melting at 197° .

The assumption that the nitro-group enters position 6 is based on the fact that the 6-nitro-derivative is formed first in the nitration of 4-methyl-1:2- α -naphthapyrone (Dey, T., 1915, 107, 1613).

ψ -Benzo-1:8-isonaphthoxazone crystallises in soft, pale yellow needles melting at 243° . The yield amounted to 30 per cent. of the weight of the nitro-compound employed:

0.1490 gave 7.8 c.c. N_2 at 24.5° and 759 mm. $N=5.9$.

$C_{10}H_9O_2N$ requires $N=5.65$ per cent.

4-Methyl- ψ -benzo-1:8-isonaphthoxazone was prepared from 6-nitro-4-methyl-1:2- α -naphthapyrone, and it exhibited the same

characteristics as the foregoing compound. The yield in one instance amounted to 50 per cent. of the theoretical.

It crystallises in pale yellow needles melting at 234°:

0.2291 gave 11.4 c.c. N₂ at 24° and 759 mm. N=5.6.

C₁₇H₁₁O₂N requires N=5.36 per cent.

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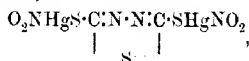
[Received, March 15th, 1919.]

XL.—Mercury Mercaptide Nitrites and their Reaction with the Alkyl Iodides. Part V. Chain Com- pounds of Sulphur (continued).

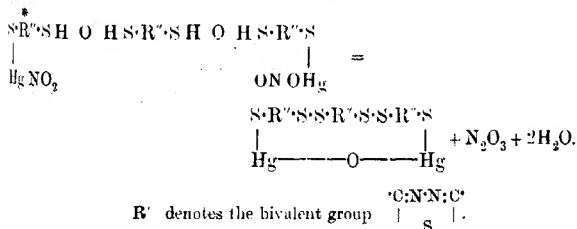
By SIR PRAFULLA CHANDRA RAY and PRAFULLA CHANDRA GUHA.

THE present series of investigations has hitherto been confined to derivatives of monomercaptans; it has now been extended to those of the dimercaptans, of which 2:5-dithiol-1:3:4-thiodiazole may be taken as a typical representative.

When this dimercaptan is treated with mercuric nitrite, a dimercaptide dinitrite,

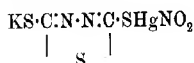


is not obtained, but the nitrous acid simultaneously disengaged oxidises the hydrogen atoms of two, three, four, and even six molecules of the dimercaptan, and the sulphur atoms become linked together and give rise to an interesting series of closed chain compounds. The maximum number of sulphur atoms forming the connecting link between two adjacent nuclei in the condensed complex molecule thus formed has so far been found to be twelve. Thus, in the case of a trinuclear condensation, we have



The heavy molecule of the dimercaptide dinitrite cannot retain the load of two NO_2 groups, and hence rupture takes place, as indicated by the dotted line, and a closed chain sulphony-derivative is finally formed with the liberation of nitrous fumes. The compounds thus generated are not, as a rule, nitrites. Some preparations, however, responded slightly to the nitrite tests, but the percentage of nitrogen due to the presence of nitrite was very low, proving that the proportion of the latter was insignificant. The occasional presence of some nitrite goes to establish the fact that the oxy-compound is in reality a decomposition product of the former.

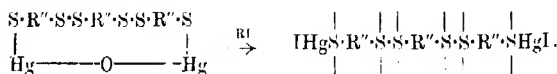
If, instead of the dimercaptan itself, its potassium salt is used, the tendency towards oxidation by nitrous acid is excluded and a mercaptide nitrite of the formula



is obtained.

The sulphony-compounds may be represented by the general formula $(\text{C}_2\text{N}_2\text{S}_2)_x\cdot\text{Hg}_2\text{O}$, where $x=2, 3, 4$, or 6. A condensation product of five molecules has not yet been obtained. It is not easy to explain why in one operation the value of x should be two and in others it should rise to six; possibly the concentration of the parent substances is the main determining factor. It has often been found that two preparations under similar conditions had identical compositions. In the majority of cases, the value of x was found to be three, occasionally two and four, and only rarely six.

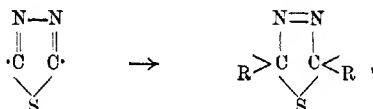
The preparations could not have been admixtures, because each of them strictly conformed to a definite formula. The most convincing proof of these compounds being of definite composition, however, is afforded by their reaction with the alkyl iodides. These sulphony-compounds behave exactly like mercaptide nitrites, and yield, as a rule, the corresponding sulphonium derivatives and, in a few cases, those with a less number of nuclei. The reducing action of the alkyl iodide removes the oxygen atom of the sulphony-ring, and, the bonds being thus snapped, an open-chain compound is formed, thus:



The six sulphur atoms of the chain now become quadrivalent by taking up the components of the alkyl iodide.

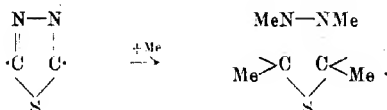
In this manner, a series of tetra-, hexa-, octa-, and dodeca-sulphonium compounds have been prepared. Each of these, with the exception of the propyl and butyl derivatives, is characterised by its crystalline character, and, moreover, its successive crops have the same melting point; the possibility of their being mixtures is thus precluded.

Another interesting point is the shifting of the double bonds, thus:



where R=methyl, ethyl, propyl, or butyl. As a rule, this is confined only to one nucleus. There is here evidently an extension of Thiele's theory to nitrogen compounds.

In one isolated instance, and that in the case of the reaction with methyl iodide, instead of there being a shifting of the double bonds, both the pairs of nitrogen and carbon atoms throughout the molecule were saturated by taking up additional methyl groups, thus:



EXPERIMENTAL.

Sulphony-compounds.

General Method of Preparation.—2:5-Dithiol-1:3:4-thiodiazole, prepared according to Busch's method (*Ber.*, 1894, **27**, 2518), in dilute alcoholic solution, was added drop by drop with vigorous stirring to a solution of mercuric nitrite, care being taken that the latter was always in excess. In this manner, a semi-gelatinous, pale yellow precipitate was obtained, which was washed with water and dried in a vacuum desiccator. The powdered, granular mass was then heated under reflux successively with alcohol and benzene to remove any adhering accidental organic impurities, namely, the parent dimercaptan or its oxidation product, the disulphide. This precaution was, however, found to be unnecessary. The compounds obtained in this way are always associated with some molecules of water.

Potassium Salt of 2:5-Dithiol-1:3:4-thiodiazole and Mercuric Nitrite.

With an aqueous solution of the potassium salt, a compound of the formula

$$\begin{array}{c} \text{KS}\cdot\text{C}\cdot\text{N}\cdot\text{N}\cdot\text{C}\cdot\text{SHgNO}_2 \\ | \quad \text{S} \end{array}$$

with $12\text{H}_2\text{O}$ is obtained. Analysis of the substance gave:

Found: Hg=31.50; S=13.89; C=3.53; H=5.34.*

$\text{C}_2\text{O}_2\text{N}_2\text{S}_2\text{HgK}\cdot 12\text{H}_2\text{O}$ requires Hg=30.81; S=14.79; C=3.70; H=3.70 per cent.

2:5-Dithiol-1:3:4-thiodiazole and Mercuric Nitrite: Formation of

the Dinuclear Sulpho-xy compound.

$$\begin{array}{c} \text{S}\cdot\text{C}_2\text{N}_2\text{S}\cdot\text{S}_2\cdot\text{C}_2\text{N}_2\text{S}\cdot\text{S} \\ | \quad \quad \quad | \\ \text{Hg} \text{---} \text{O} \text{---} \text{Hg} \end{array} \cdot 3\text{H}_2\text{O}.$$

Found: Hg=52.57, 52.42; S=23.76; N=7.36.

$(\text{C}_4\text{ON}_4\text{S}_6\text{Hg}_2)\cdot 3\text{H}_2\text{O}$ requires Hg=52.22; S=25.07; N=7.31 per cent.

Trinuclear Sulpho-xy-compound,

$$\begin{array}{c} \text{S}\cdot\text{C}_2\text{N}_2\text{S}\cdot\text{S}_2\cdot\text{C}_2\text{N}_2\text{S}\cdot\text{S}_2\cdot\text{C}_2\text{N}_2\text{S}\cdot\text{S} \\ | \quad \quad \quad | \quad \quad \quad | \\ \text{Hg} \text{---} \text{O} \text{---} \text{Hg} \end{array}$$

* In this case, each distinct preparation gave the compound associated with 8, 5, and 2 molecules of water respectively.

Compound with 8H₂O.

Found: Hg=40.21; S=27.56; C=8.50; N=8.18.

$\text{C}_6\text{ON}_6\text{S}_9\text{Hg}_3\cdot 8\text{H}_2\text{O}$ requires Hg=39.85; S=28.69; C=7.17; N=8.37 per cent.

Compound with 5H₂O.

Found: Hg=42.07; S=30.21; N=9.36.

$\text{C}_6\text{ON}_6\text{S}_9\text{Hg}_3\cdot 5\text{H}_2\text{O}$ requires Hg=42.11; S=30.31; N=8.84 per cent.

Compound with 2H₂O.

Found: Hg=45.33; S=31.40; N=9.52.

$\text{C}_6\text{ON}_6\text{S}_9\text{Hg}_3\cdot 2\text{H}_2\text{O}$ requires Hg=44.65; S=32.14; N=9.38 per cent.

On repeating the preparation, the same trinuclear condensation

* The percentage of hydrogen is often too high as traces of mercury vapour are apt to be carried over to the calcium chloride tube; in many cases, therefore, the value of hydrogen has not been given.

product was obtained, although sometimes in an impure form. Thus in one preparation there was found $\text{Hg}=42.52$, $\text{S}=34.54$, and in another, $\text{Hg}=43.72$, $\text{S}=31.53$. However, on treating each of these with the alkyl iodides, the same sulphonium compound was obtained (see p. 546).

Tetranuclear Sulphoxy-compound, $(\text{C}_2\text{N}_2\text{S}_3)_4, \text{Hg}_2\text{O}$.

Compound with $3\text{H}_2\text{O}$.

Found: $\text{Hg}=37.94$; $\text{S}=37.54$; $\text{N}=11.48$.

$\text{C}_8\text{ON}_8\text{S}_{12}\text{Hg}_2, 3\text{H}_2\text{O}$ requires $\text{Hg}=37.67$; $\text{S}=36.16$; $\text{N}=10.55$ per cent.

Compound with $5\text{H}_2\text{O}$.

Found: $\text{Hg}=37.21$; $\text{S}=35.13$; $\text{N}=9.55$.

$\text{C}_8\text{ON}_8\text{S}_{12}\text{Hg}_2, 5\text{H}_2\text{O}$ requires $\text{Hg}=36.43$; $\text{S}=34.97$; $\text{N}=10.2$ per cent.

Hexanuclear Sulphoxy-compound, $(\text{C}_2\text{N}_2\text{S}_3)_6, \text{Hg}_2\text{O}, 7\text{H}_2\text{O}$.

Found: $\text{Hg}=28.52$; $\text{S}=39.82$; $\text{N}=11.59$.

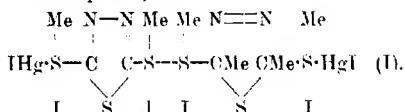
$\text{C}_{12}\text{ON}_{12}\text{S}_{18}\text{Hg}_2, 7\text{H}_2\text{O}$ requires $\text{Hg}=27.97$; $\text{S}=40.28$; $\text{N}=11.75$ per cent.

Reaction with the Alkyl Iodides.

General Method of Preparation.—The above sulphony-derivatives were heated with the alkyl iodides on a water-bath under reflux for several hours, the product being allowed to remain overnight. Sometimes a crystalline mass, and occasionally a heavy, dark brown oil, settled at the bottom; the excess of alkyl iodide was decanted or distilled off, and the product dissolved in the minimum quantity of acetone and the solution filtered from the insoluble matter whenever necessary. On adding ether to the filtrate, a pale yellow, mealy, crystalline precipitate was obtained, and this process was repeated in order further to purify the substance.

Dinuclear Condensation.

The Compound, $\text{C}_4\text{ON}_4\text{S}_8\text{Hg}_2$, and Methyl Iodide: Formation of the Compound,



The product melted at $101\text{--}102^\circ$.

Found: Hg=25.94; I=49.23; C=7.75.

$C_{10}H_{13}N_4S_6Hg_2I_6$ requires Hg=25.84; I=49.33; C=7.75 per cent.

The corresponding compound with ethyl iodide (II) was sparingly soluble in acetone, and was therefore purified by crystallisation from the boiling solvent; it melted at 107°.

Found: Hg=24.19, 24.58; I=43.20*; C=11.25, 11.42; N=3.53, $C_{16}H_{30}N_4S_6Hg_2I_6$ requires Hg=24.51; I=46.69; C=11.76; N=3.43 per cent.

The corresponding dinuclear tetrasulphonium compounds with *n*-propyl and *n*-butyl iodides did not crystallise, but consisted of dark brown, pasty masses, which were purified by repeated precipitation with ether from acetone solution.

Compound with n-propyl iodide (III).

Found: Hg=23.89; I=44.74; C=14.05.

$C_{22}H_{42}N_4S_6Hg_2I_6$ requires Hg=23.31; I=44.40; C=15.38 per cent.

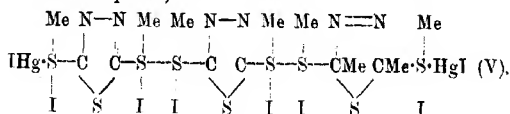
Compound with n-butyl iodide (IV).

Found: Hg=21.77; I=41.75; C=17.66; N=3.11.

$C_{23}H_{34}N_4S_6Hg_2I_6$ requires Hg=22.22; I=42.33; C=18.60; N=3.11 per cent.

Trinuclear Condensation.

The Compound, $C_6ON_6S_6Hg_2$, and Methyl Iodide: Formation of the Compound,



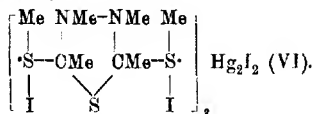
The product of the interaction was an oil. It was dissolved in hot acetone, and the solution, on cooling, deposited a crystalline mass, which when recrystallised from hot acetone yielded needle-shaped crystals melting at 101–102°, identical with the compound, $C_{10}H_{13}N_4S_6Hg_2I_6$, described above. The original mother liquor, on concentration, gave two successive crops melting at 85–86°.

Found: Hg=21.55; C=8.66.

$C_{14}H_{24}N_6S_6Hg_2I_6$ requires Hg=20.20; C=8.48 per cent.

* As a large quantity of copper powder has to be used and the process is a tedious one, the values for iodine and sulphur are sometimes too low (see T., 1916, 109, 611).

Compound with Methyl Iodide in which all the Double Bonds are Saturated,



The method of preparation and purification was the same as in the case of the preceding compound. It is a white, crystalline substance melting at 94° .

Found: Hg=18.24; S=11.36; C=13.15; H=2.54.

$\text{C}_{24}\text{H}_{64}\text{N}_6\text{S}_9\text{Hg}_2\text{I}_8$ requires Hg=18.78; S=13.52; C=13.52; H=2.53 per cent.

The formation of this type of compound has been observed only in this one instance.

Compound with n-Propyl Iodide (VII).

This conforms to the ordinary type.

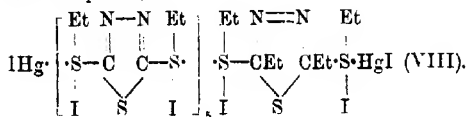
Found: Hg=18.54; I=44.61; C=16.47.

$\text{C}_{39}\text{H}_{56}\text{N}_6\text{S}_9\text{Hg}_2\text{I}_8$ requires Hg=18.14; I=46.1; C=16.33 per cent.

As will be noticed, the trinuclear sulphonyl-compound gives with methyl iodide compounds I and V, the latter being the chief product. This tendency towards the formation of the dinuclear tetra-sulphonyl compound from the higher nuclear sulphonyl-compounds is particularly noticeable in the case of the reaction with ethyl iodide, when only the dinuclear sulphonyl compound (II) is obtained, even from tri- and tetra-nuclear sulphonyl-derivatives. In all these cases of formation of a lower member from the higher sulphonyl-compounds, a dark brown, pasty substance with a penetrating odour and lachrymatory properties was always produced, which resisted all attempts at purification.

Hexanuclear Condensation.

The Compound, $\text{C}_{12}\text{ON}_{12}\text{S}_{15}\text{Hg}_2$, and Ethyl Iodide: Formation of the Compound,



This melted at $90\text{--}91^\circ$.

Found: I=50.03; N=3.90; C=13.14.
 $C_{40}H_{70}N_{12}S_{18}Hg_2I_{14}$ requires I=51.20; N=4.84; C=13.82 per cent.

It will thus be seen that the type persists throughout, in that the alteration in the position of the double bond is limited to only one nucleus of the chain.

In the previous communications, the compounds there described were tentatively classed under the sulphonium group, although no direct proof could be adduced in support of this view. One of the purest compounds of this series, namely, $MeEtS_2, HgI_2, EtI$ (T., 1916, 109, 606), was selected for molecular weight determination in acetone solution by the ebullioscopic method; the value obtained was 712, that required by theory being 718. It is thus evident that the constitution is atomic (compare Hilditch and Smiles, T., 1907, 91, 1396).

A study of the physical properties of the interesting polysulphonium compounds treated of in this paper is being undertaken which, it is hoped, will throw additional light on their constitution.

CHEMICAL LABORATORY,
 COLLEGE OF SCIENCE,
 UNIVERSITY OF CALCUTTA.

[Received, November 30th, 1913.]

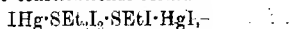
XLI.—Mercury Mercaptide Nitrites and their Reaction with the Alkyl Iodides. Part VI. Chain Compounds of Sulphur (continued).

By SIR PRAFULLA CHANDRA RÂY.

THE present investigation deals with the chain compounds of sexavalent sulphur. On treating the product of the interaction of thiocarbamide and mercuric nitrite, namely, the sulphoxynitrite,

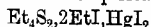
$NH_2 \cdot C:(NH) \cdot S(HgNO_2) < \overset{Hg}{\underset{O}{\parallel}}$ (T., 1917, 111, 102), with ethyl

iodide, a yellow, crystalline substance was obtained which was soluble in acetone, and, on purification by precipitation with ether, melted at 98—100°. Analysis proved it to conform to the formula $Et_2S_2, EtI, 2HgI_2$; in other words, it is a member of the disulphonium series already described (T., 1916, 109, 134) with an additional molecule of mercuric iodide in combination, to which should be assigned the constitutional formula



one of the sulphur atoms in the chain becoming sexavalent. The formation of this compound suggested the possibility of the direct conversion of all the members of the series $RR/S_2R/I, HgI_2$ into $RR/S_2R/I, 2HgI_2$. This anticipation has been realised with one notable exception. When the alkyl group happens to be methyl, combination with an extra molecule of mercuric iodide does not take place. The presence of the radicle ethyl, on the other hand, favours the combination. Thus in the above series, where $R = Me$ and $R' = Pr$ or butyl, the extra valencies of the sulphur atom are not revived, but if R' happens to be ethyl, this anomaly disappears. To what extent the ethyl group favours the increase in valency will be evident from a typical case. When mercury ethyl-mercaptide nitrite, $EtS \cdot HgNO_2$, is treated with methyl iodide, by an interchange of the radicle, the compound, $EtMeS_2, HgI_2, MeI$, is obtained (T., 1916, 109, 603); but in this case, although there are two methyl groups, the presence of a single ethyl group is sufficient to counteract the prejudicial influence of the former, and the compound, $EtMeS_2, MeI, 2HgI_2$, is readily formed.

The marked genetic affinity of the radicle ethyl for sulphur and its influence on the increase in its valency is further evidenced by the fact that a compound of the empirical formula



has also been obtained from ethyl sulphide by its reaction with ethyl iodide and mercuric iodide. On repeating Smiles's experiment (T., 1900, 77, 161), under slightly altered conditions, with a view to ascertain the maximum valency of sulphur, it was noticed that whilst the main product was the compound, Et_3SI, HgI_2 , as found by this author, there was always a considerable amount of a shining, crystalline substance, practically insoluble in cold acetone. As it had a sharp melting point when crystallised from hot acetone, it was analysed, with the result that the formula given above was established. What evidently happens is that under the joint action of mercuric iodide and ethyl iodide, or rather their ions, the bivalent sulphur atoms of two adjacent molecules of ethyl sulphide become sexavalent, with the formation of the compound, $SEt_3I_2 \cdot SEt_3I \cdot HgI$.

It is remarkable that if, in the above reaction, ethyl iodide is substituted by methyl, propyl, or butyl iodide, the product in each case is completely soluble in acetone and conforms to the general formula Et_3RSI, HgI_2 , but no product of the fusion of two ethyl sulphide molecules is formed. The differential property of ethyl as compared with other alkyl radicles is thus brought into relief.

It was expected that the general method of the preparation of

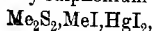
the disulphonium compounds already described, namely, the treatment of ethyl mercurimercaptide nitrite, EtS.HgNO_2 , with ethyl iodide, should also yield the chain compound containing both the sulphur atoms in the sexavalent state. This expectation has also been realised. The latter compound is produced in such small amount that on previous occasions its formation was overlooked. It has already been shown that ethyl disulphide, ethyl iodide, and mercuric iodide also combine directly to yield the disulphonium compound, $\text{Et}_2\text{S}_2\text{HgI}_2\text{EtI}$ (*loc. cit.*). Recently, this preparation has been repeated, and it has been found that the sexavalent disulphur compound is also formed in considerable quantity along with the former. It is thus evident that both the chain compounds, containing quadri- and sexa-valent sulphur respectively, are formed simultaneously.

It is of interest to note that Smiles and Hilditch, who treated an acetone solution of molecular proportions of ethyl disulphide and mercuric iodide with ethyl iodide, obtained diethylthioethylsulphonium dimercuric iodide, $(\text{C}_2\text{H}_5)_3\text{S}_2\text{I}_2\text{HgI}_2$ (T., 1907, 91, 1396). It is evidently the same compound as has been described above.

An explanation may be offered as to why it is that in the first series of compounds only one of the two atoms of sulphur exists in the sexavalent condition; here the quadrivalent sulphur, being already weighted with the heavy load of the ions HgI' and I' , has lost the capacity of taking up an additional charge; in other words, of acquiring the maximum valency. In the solitary instance, however, in which both the sulphur atoms happen to be sexavalent, it will be noticed that there is only one set of HgI' and I' ions; the sulphur atom combined with the latter has attached to it three additional comparatively light ethyl radicles, whereas the other sulphur atom, not having to bear the load of the heavy HgI -group, is in a position to take up three ethyl groups and two iodine atoms. Facts are already known which go to support the view that the maximum valency of an element is often conditional on the load of the radicles. The author hopes in a succeeding communication to show that platinum when attached to the radicle of 5-thiol-2-thio-3-phenyl-2:3-dihydro-1:3:4-thiodiazole, is in the tervalent condition. It is none the less inexplicable why the light radicle methyl should stand in the way of one of the atoms of sulphur attaining its maximum valency. The anomalous behaviour of the first member of the alkyl series is, however, well known.

EXPERIMENTAL.

The general method of preparation of the series $R_2S_2, RI, 2HgI_2$ has already been incidentally described. These members are readily obtained by dissolving the corresponding disulphonium compound in acetone and adding mercuric iodide to the solution until no more is absorbed. The golden-yellow liquid is decanted from the undissolved iodide, and, on adding ether, a copious deposit of yellow, mealy crystals is obtained. Solution in acetone and precipitation by ether is repeated until the product gives a fairly sharp melting point. It has been found that in some instances, especially in the case of the methylsulphonium compound,



the acetone solution at first takes up a considerable quantity of mercuric iodide, but purification by the above process gradually removes all the mechanically held salt.

Compound $Et_2S_2, EtI, 2HgI_2$.—(a) From the sulphoxynitrite derivative of thiocarbamide and ethyl iodide. The substance melted at 98° :

0.3656 gave 0.1250 Hg, 0.3540 AgI, and 0.1029 $BaSO_4$.
 $Hg=34.19$; $I=52.32$; $S=3.87$.

0.2442 gave 0.0570 CO_2 and 0.0356 H_2O . $C=6.37$; $H=1.62$.

(b) By the direct union of mercuric iodide with the compound Et_2S_2, EtI, HgI_2 . The substance melted at $100-101^\circ$:

0.2118 gave 0.0711 Hg. $Hg=33.57$.

0.2118 „ 0.0532 CO_2 and 0.0325 H_2O . $C=6.85$; $H=1.71$.

$C_6H_{15}I_5S_2Hg_2$ requires $Hg=33.73$; $I=53.54$; $S=5.4$; $C=6.07$;
 $H=1.26$ per cent.

Compound $MeEtS_2, EtI, 2HgI_2$ (m. p. $38-40^\circ$):

0.3840 gave 0.1236 Hg and 0.3768 AgI. $Hg=32.19$; $I=53.03$.

0.2094 „ 0.0452 CO_2 and 0.0466 H_2O . $C=5.87$; $H=2.47$.

$C_3H_{13}I_5S_2Hg_2$ requires $Hg=34.14$; $I=54.19$; $C=5.12$; $H=1.11$
 per cent.

Compound $MeEtS_2, MeI, 2HgI_2$ (m. p. $50-55^\circ$):

0.2467 gave 0.2483 AgI and 0.0840 Hg. $Hg=34.05$; $I=54.39$.

0.1428 „ 0.0286 CO_2 and 0.0211 H_2O . $C=5.46$; $H=1.64$.

$C_4H_{11}I_5S_3Hg_2$ requires $Hg=34.55$; $I=54.84$; $C=4.14$; $H=0.95$
 per cent.

Compound $EtPr^*S_2, Pr^*I, 2HgI_2 + C_3H_6O$ (m. p. $30-31^\circ$).—This compound contains one molecular proportion of acetone:

0.4410 gave 0.1400 Hg. $\text{Hg} = 31.75$.

0.1629 „ 0.0586 CO_2 and 0.0352 H_2O . $\text{C} = 9.81$; $\text{H} = 2.40$.

$\text{C}_8\text{H}_{19}\text{I}_5\text{S}_2\text{Hg}_2, \text{C}_3\text{H}_6\text{O}$ requires $\text{Hg} = 31.45$; $\text{C} = 10.38$; $\text{H} = 1.97$
per cent.

Compound $\text{Et}(\text{C}_4\text{H}_9)_2\text{S}_2, \text{C}_4\text{H}_9\text{I}, 2\text{HgI}_2 + 1.5\text{C}_3\text{H}_6\text{O}$.—The substance had the consistency of treacle, and contained 1.5 molecular proportions of acetone:

0.3879 gave 0.1153 Hg and 0.3272 AgI. $\text{Hg} = 29.72$; $\text{I} = 45.58$.

0.1340 „ 0.0649 CO_2 and 0.0363 H_2O . $\text{C} = 13.21$; $\text{H} = 3.01$.

$\text{C}_{10}\text{H}_{23}\text{I}_5\text{S}_2\text{Hg}_2, 1.5\text{C}_3\text{H}_6\text{O}$ requires $\text{Hg} = 30.10$; $\text{I} = 47.79$; $\text{C} = 13.10$;
 $\text{H} = 2.41$ per cent.

Compound containing two sexavalent sulphur atoms (m. p. $146-147^\circ$). It was very sparingly soluble in cold acetone, but fairly readily so in the boiling solvent:

0.2991 gave 0.063 Hg and 0.2916 AgI. $\text{Hg} = 21.06$; $\text{I} = 52.69$.

0.4032 „ 0.8400 Hg and 0.2042 BaSO_4 . $\text{Hg} = 20.86$; $\text{S} = 6.96$.

0.1930 „ 0.1068 CO_2 and 0.0538 H_2O . $\text{C} = 15.09$; $\text{H} = 3.09$.

$\text{C}_{12}\text{H}_{30}\text{I}_4\text{S}_2\text{Hg}$ requires $\text{Hg} = 21.14$; $\text{I} = 53.70$; $\text{S} = 6.77$; $\text{C} = 15.22$;
 $\text{H} = 3.17$ per cent.

CHEMICAL LABORATORY,
COLLEGE OF SCIENCE,
UNIVERSITY OF CALCUTTA.

[Received, January 8th, 1919.]

XLII.—Mercuric Sulphoxychloride.

By SIR PRAFULLA CHANDRA RAY and PRAFULLA KUMAR SEN.

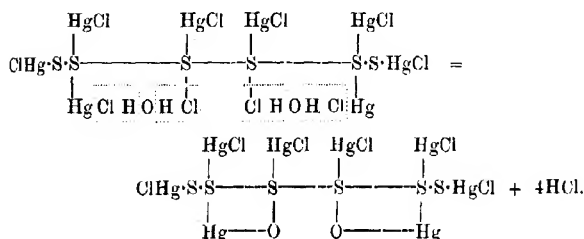
THE close analogy between mercuric chloride and nitrite has been found to hold good throughout the investigations carried on from 1898 onwards. Thus, whilst mercuric nitrate with sodium sulphate at once gives an abundant yellow precipitate of the oxysulphate, the chloride and the nitrite fail to give it (T., 1897, **71**, 1103). The explanation lies in the fact that the latter salts are very feebly ionised in solution, and thus have no tendency to yield basic compounds. Ammonia, amines, and even a class of alkaloids have been found to behave towards mercuric nitrite in a manner similar to their action on the chloride (T., 1913, **103**, 3; 1917, **111**, 507).

The substituted thiocarbamides, thiocarbimides, thiobenzamide, etc., have been shown to give rise to a purely inorganic sulphony-nitrite of the empirical formula $[\text{3}(\text{SHgNO}_2), \text{HgO}]_2$, which is in

reality a chain compound containing six atoms of sulphur linked together (T., 1917, 111, 104).

An attempt has been made to isolate the radicle $(\text{SHgCl})_2$, which would be the analogue of mercuric iodosulphide, $(\text{SHgI})_2$ (*loc. cit.*, p. 109), by treating mercuric chloride with some typical thio-compounds named above, as also thioacetic acid and ammonium dithiocarbamate. It was expected that in each case the radicle, SHgCl , would become detached from the parent substance and lead an independent existence. This expectation has been realised, but in a qualified sense. The radicle, SHgCl , no sooner separates out than it assumes the form $[3(\text{SHgCl}), \text{HgO}]_2$, which is the exact analogue of the oxynitrite. It has been shown already that the complex nitrite containing several nitro-groups, by the elimination of nitrogen trioxide, readily yields the oxynitrite.

It is not easy at first to understand how the chloride would also give rise to an oxy-salt. The explanation is obvious when it is considered that water takes part in the reaction; the compound $[3(\text{SHgCl}), \text{HgO}]_2$ is formed thus:

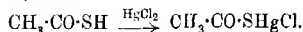


In other words, as soon as the radicle, SHgCl , is formed, three groups take up an additional molecule of mercuric chloride, that is, the radicles HgCl and Cl and a molecule of water simultaneously take part in the reaction, four molecules of hydrogen chloride are generated, and the oxygen atom forms the connecting link between the mercury atom, the neighbouring sulphur atom, and the two symmetrical complexes coalescing into a single molecule.

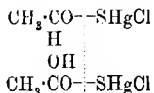
It is necessary to point out that whilst the radicle, SHgNO_2 , has often a tendency to part company with the parent substance, the radicle, SHgCl , on the other hand, often remains attached to it. Thus thiocarbamide when acted on by mercuric chloride yields the compound $\text{NH}_2\text{C}:\text{NH}\cdot\text{SHgCl}, \text{HCl}$, which is actually a hydrochloride, as will be shown in a subsequent communication. If, however, thiocarbamide is converted into its diacetyl derivative and then treated with mercuric chloride, the molecule is ruptured,

with the detachment of the radicle, SHgCl , and the formation of the oxychloride. δ -Diphenylthiocarbamide also behaves similarly. Evidently the introduction of the negative radicles, acetyl and phenyl, neutralises the basic character of the compound due to the presence of an amino- and imino-group, and deprives it of the power of forming a hydrochloride, in which character alone it is stable.

It is a characteristic diagnostic property of mercaptans, real and potential, that with mercuric nitrite and chloride they yield the mercaptide nitrite and chloro-mercaptide respectively. Thioacetic acid, although an acid, contains the group SH and behaves like a typical mercaptan, thus:



As soon as this compound is formed, it acts on a molecule of water, and the scission takes place as shown by the dotted line, a



molecule of acetaldehyde and acetic acid being formed.

Ammonium dithiocarbamate assumes the tautomeric form, $\text{SH}\cdot\text{C}(\text{NH})\cdot\text{SNH}_2$, and both the radicles SH and SNH_2 with mercuric chloride yield SHgCl , which separates out.

Allylthiocarbimide, $\text{C}_3\text{H}_5\cdot\text{NCS}$, combines with the elements of mercuric chloride, and the compound, $\text{C}_3\text{H}_5\cdot\text{N}:\text{C}:\text{SCl}\cdot\text{HgCl}$, is temporarily formed, the sulphur atom becoming quadrivalent. As this configuration is unstable, a rupture takes place along the line of least resistance, the radicle, $:\text{SCl}\cdot\text{HgCl}$, decomposes into the stable radicle, SHgCl , and chlorine, whilst the organic portion of the complex, $\text{R}\cdot\text{N}:\text{C}:$, with a molecule of water yields a primary amine and carbon monoxide.

EXPERIMENTAL.

Method of Preparation.—The thio-compound in aqueous or alcoholic solution, as the case might be, was added in a thin stream by means of a pipette to an aqueous solution of mercuric chloride with vigorous stirring, care being taken that the latter ingredient was always in large excess.

A granular, white precipitate was obtained, which was washed first with water and then with alcohol, and finally dried in a vacuum over sulphuric acid. A special precaution is necessary in the case of allylthiocarbimide. If an alcoholic solution of it is

added to an aqueous solution of mercuric chloride, the white precipitate is obtained, but, at the same time, heavy, oily globules begin to settle down at the bottom, and it is not always easy to separate them from the sulphoxychloride. It is best to add the dilute alcoholic solution of the allylthiocarbimide to an alcoholic solution of mercuric chloride. The mixture remains clear, but on copious dilution with water and stirring, the white precipitate begins to appear. The mixture is allowed to remain overnight, and the product collected and treated as before.

The interaction of each of the above-mentioned thio-compounds and mercuric chloride was repeated several times, and the composition throughout was found to be identical. It is therefore not necessary to give the analysis of each preparation; that of one or two typical ones are given below.

Action of Mercuric Chloride on Diacetylthiocarbamide.

Diacetylthiocarbamide (Kohmann, *J. Amer. Chem. Soc.*, 1915, 37, 2130) was dissolved in water and added drop by drop to a solution of mercuric chloride from a pipette with constant stirring. A white, amorphous precipitate was formed which, on remaining for twenty-four hours, became granular. It was collected, washed with water, and dried:

0.3276 gave 0.2591 Hg and 0.1354 AgCl. Hg=79.1; Cl=10.2.
0.2419 „ 0.1048 AgCl and 0.1647 BaSO₄. Cl=10.7; S=9.4.
[3(SHgCl),HgO]₂ requires Hg=78.7; Cl=10.5; S=9.4 per cent.

The absence of carbon and hydrogen was confirmed by repeated combustion.

Action of Mercuric Chloride on s-Diphenylthiocarbamide.

The hot alcoholic solution of s-diphenylthiocarbamide was added to a solution of mercuric chloride, and the mixture was heated in a boiling-water bath under reflux for several hours. The white precipitate was collected, washed with hot alcohol and finally with water, and dried:

0.2591 gave 0.1097 AgCl and 0.1698 BaSO₄. Cl=10.47; S=9.0.
0.3684 „ 0.2902 Hg. Hg=78.8.

Mercuric Chloride and Thioacetic Acid.

Result of analysis:

0.2587 gave 0.2370 HgS. Hg=79.0.
0.1465 „ 0.0625 HgCl and 0.1070 BaSO₄. Cl=10.55;
S=10.0.

*Mercuric Chloride and Allylthiocarbimide.**Result of analysis:*

0.3402 gave 0.2631 Hg. Hg=77.34.

0.2795 „ 0.1285 AgCl and 0.1818 BaSO₄. Cl=11.4; S=8.9.

The absence of carbon was shown by combustion analysis.

CHEMICAL LABORATORY,
COLLEGE OF SCIENCE,
UNIVERSITY OF CALCUTTA.

[Received, October 15th, 1918.]

XLIII.—*The Preparation of Cadmium Suboxide.*

By HENRY GEORGE DENHAM.

VARIOUS suboxides of cadmium have long ago been described (Tanatar, *Zeitsch. anorg. Chem.*, 1901, **27**, 433; Morse and Jones, *Amer. Chem. J.*, 1890, **12**, 488, etc.), although other investigators have thrown doubt on the existence of these suboxides. The following experiments describe the efforts made to prepare a suboxide of cadmium in as pure a state as has been the case with lead suboxide.

Decomposition of Cadmium Oxalate.

The first method attempted was that described by Tanatar (*loc. cit.*), namely, the decomposition of the oxalate in a stream of carbon dioxide. A sample of cadmium oxalate (Cd=56.02 per cent.) was heated at 300° in a rapid stream of carbon dioxide freed from traces of oxygen by passage through heated copper. At the end of forty-eight hours the evolution of gas ceased, and examination revealed a small quantity of a green material, unmistakably containing globules of cadmium, whilst the leading tubes were lined with a deposit of the volatilised metal. This experiment, many times repeated, always gave the same result.

Precisely similar results were obtained when the carbon dioxide was not employed, the evolved gases being removed by means of a Sprengel pump. Even when the total pressure of these gases did not exceed 1 mm., the same green, heterogeneous substance was produced. Analysis of this material always gave values closely approximating to Cd=96.5 per cent. (Tanatar's Cd₄O contains Cd=96.56 per cent.).

Tanatar and Levin (*loc. cit.*) also describe how the oxide, Cd_2O , was obtained by the decomposition of a basic oxalate under similar conditions. A repetition of their experiment always gave a heterogeneous grey mass containing free cadmium.

An attempt was then made to remove by distillation the excess of metal present in the decomposition product of the oxalate. The mixture was heated to 350° without undergoing any change in appearance. The pump was then put into requisition, and in ten hours a large deposit of cadmium had volatilised out of the oven, whilst the residue was a homogeneous green mass, in which the microscope was no longer able to detect free metal. The following analytical results were obtained:

| Oxalate. Grams. | Green substance. Gram. | CdSO_4 . Gram. | Cd. per cent. |
|--------------------|---------------------------|----------------------------|------------------|
| 2.0 | 0.0362 | 0.0628 | 93.5 |
| 2.5 | 0.0592 | 0.1025 | 93.4 |
| 2.0 | 0.0809 | 0.1401 | 93.4 |

Cd_2O requires $\text{Cd} = 93.36$ per cent.

The method therefore appears to give a green oxide, but owing to the strong reducing action of the evolved carbon monoxide and the difficulty of distilling out the free metal, the method is not satisfactory.

Reduction by Hydrogen.

An attempt was made to prepare the suboxide by reducing the brown oxide with hydrogen (see Glaser, *Zeitsch. anorg. Chem.*, 1903, **36**, 1). At 240° , after twenty hours' reduction, the yellowish-green product appeared to be uniform, but the microscope clearly revealed globules of free metal. Reduction under varying conditions of temperature and pressure always led to this result. The excess of metal was afterwards removed by distillation, and a uniform, yellowish-green product obtained, in which the microscope revealed no sign of free metal. Analysis, however, showed that this substance was pure cadmium oxide (CdO), the colour change being either superficial or due to a different molecular aggregation.

Reduction by Carbon Monoxide.

It has been shown by Brislee (T., 1908, **93**, 162) that the time-reduction curve of cadmium oxide at 300° , with carbon monoxide as the reducing agent, shows a distinct break at a point which corresponds with the compound Cd_2O . Although it appeared

difficult to stop the reduction at the precise moment when the whole of the higher oxide had been reduced to the suboxide and none of the latter to the metal, it seemed feasible to carry through the reduction in such a way that the higher oxide was reduced to a mixture of the suboxide and metal, and this metal could then be removed by volatilisation.

An analysis of Brislee's time-reduction curve for 300° shows that the break occurs when the reduction has progressed for about twelve hours. An experiment was therefore carried out in which carbon monoxide was circulated for fourteen hours at 300° through two bulbs, each containing about 0.6 gram of cadmium oxide. One bulb was then sealed off, and the other heated in a vacuum for eighteen hours. The material in the first bulb was yellowish-green, containing visible globules of cadmium, whilst the second bulb gave a perfectly uniform, yellowish-green substance. Bulb I contained $\text{Cd}=90.4$ and bulb II $\text{Cd}=87.5$, whilst CdO requires $\text{Cd}=87.57$ per cent. This experiment was repeatedly carried out at various temperatures between 300° and 310° , and in all cases the bulb sealed off before exhaustion contained a considerably higher percentage of cadmium than does CdO , approximating often to that of Cd_2O , but a moderately good pocket lens was sufficient in every case to show that the reduction product was heterogeneous and contained cadmium. Similarly, the bulb from which the excess of cadmium had been volatilised at the temperature of the experiment always gave a uniform, yellowish-green product exactly similar to that obtained when hydrogen was the reducing agent, and the composition of this was undoubtedly that of CdO . As a means of preparation of cadmium suboxide, this method therefore fails.

Morse and Jones's Method.

Morse and Jones (*loc. cit.*) have described how anhydrous cadmium chloride, when fused with cadmium, gives a product having the composition Cd_4Cl_7 . This they consider to be possibly a mixture of $3\text{CdCl}_2 + \text{CdCl}$. On treatment with water, the product gave cadmous hydroxide, from which yellow cadmous oxide, Cd_2O , was readily obtained by dehydration. The author has repeated this work, and succeeded in reproducing the results described by Morse and Jones, but in spite of close attention to the details given in the original publication, he has never succeeded in converting more than 5 per cent. of the original chloride into suboxide, so that, as a practical method of preparing the suboxide in quantity, the method is not satisfactory.

In conclusion, it may be stated that the suboxide of cadmium may be obtained in small quantity by the method described by Morse and Jones, as well as by the decomposition of cadmium oxalate. The latter method, however, is only of use when the excess of metal, always formed during the decomposition, is distilled off in a vacuum, but the amount of residual cadmium suboxide is never more than 4 per cent. by weight of the original oxalate.

The author desires to place on record his appreciation of the facilities placed at his disposal by the Walter and Eliza Hall Trust for the prosecution of this research.

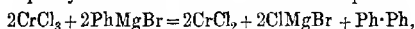
THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF QUEENSLAND,
BRISBANE.

[Received, November 7th, 1918.]

XLIV.—*Formation of Diphenyl by the Action of Cupric Salts on Organometallic Compounds of Magnesium.*

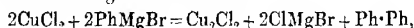
By JACOB KRIZEWSKY and EUSTACE EBENEZER TURNER.

A FEW years ago, it was shown (Bennett and Turner, T., 1914, 105, 1057) that chromic chloride reacted quantitatively with magnesium phenyl bromide in the sense of the equation



and the reaction was found to be a general one.

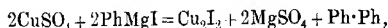
It has now been found that anhydrous cupric chloride behaves similarly to chromic chloride. Thus, when anhydrous cupric chloride is added to an ethereal solution of magnesium phenyl bromide, the following reaction occurs:



diphenyl being formed in almost the theoretical quantity. Furthermore, the preparation may be simplified, an equally good result being obtained by mixing, at the outset, magnesium turnings, ether, bromobenzene, and cupric chloride in the requisite proportions.

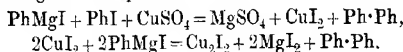
The anhydrous cupric chloride used was either the commercial preparation or that obtained by dehydrating the hydrated salt at 100°.

Anhydrous cupric sulphate reacts slowly with magnesium phenyl iodide, cupric iodide apparently being formed as an intermediate compound. It is hoped that this will ultimately lead to the preparation of cupric iodide. The reactions summed up by the equation



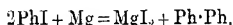
however, only proceed with difficulty, partly owing, no doubt, to the very sparing solubility of the anhydrous salt in ether.

In the presence of iodobenzene, a steady reaction occurs, probably according to the equations

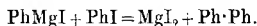


Thus when anhydrous cupric sulphate (1 mol.) is added to an ethereal solution of magnesium (2 atoms) and iodobenzene (3 mols.), a 65—70 per cent. yield of diphenyl is obtained.

Comparative experiments showed that the diphenyl produced was due neither to initial interaction of the magnesium and iodobenzene,



nor to interaction between magnesium phenyl iodide and iodobenzene,



The reactivity of cupric sulphate with magnesium phenyl iodide seems to depend on the instability of the cupric iodide formed. Magnesium phenyl bromide does not react with cupric sulphate under similar conditions.

EXPERIMENTAL.

Action of Anhydrous Cupric Chloride on Magnesium Phenyl Bromide.

Magnesium turnings (4.9 grams) were covered with 150 c.c. of pure ether, 28 grams of anhydrous cupric chloride and then 32 grams of bromobenzene were added, and the mixture was well shaken. A vigorous reaction set in, and was controlled, when necessary, by shaking and external cooling. When the initial reaction had subsided, the mixture was heated under reflux in warm water for two hours, cooled, decomposed with ice and water, and treated with excess of concentrated hydrochloric acid in order to redissolve the precipitated cuprous chloride. The ethereal layer was separated, and the aqueous layer extracted repeatedly with ether. The united ethereal extracts were shaken with water to

precipitate the cuprous chloride remaining dissolved in the acidic ethereal solution, dried, and the solvent evaporated. Thirteen grams (that is, about 85 per cent. of the theoretical) of pure diphenyl were obtained.

Using 100 c.c., and 55 c.c. of ether instead of the 150 c.c. used above, yields of 65 and 50 per cent., respectively, were obtained. An increase in the volume of ether to 200 c.c. was not found to be advantageous.

Interaction of Iodobenzene and Magnesium Phenyl Iodide.

Magnesium (4.9 grams), iodobenzene (41 grams), and ether (200 c.c.) were converted into the Grignard reagent, which was treated with 41 grams of iodobenzene, and the mixture heated under reflux for several hours. The product, on decomposition, gave 2.5 grams of diphenyl, half the iodobenzene used being recovered unchanged.

Interaction of Anhydrous Cupric Sulphate and Magnesium Phenyl Iodide.

Anhydrous cupric sulphate (32 grams) was added to the Grignard reagent, prepared from 41 grams of iodobenzene, 4.9 grams of magnesium, and 200 c.c. of ether, the mixture boiled for six hours under reflux, and then left overnight. On working up the product, 6 grams of diphenyl were obtained, corresponding with a 39 per cent. yield on the iodobenzene used.

Interaction of Cupric Sulphate (1 mol.), Magnesium (2 atoms), and Iodobenzene (3 mols.) in Ethereal Solution.

Magnesium turnings (4.9 grams) were dissolved in 200 c.c. of pure ether in the presence of 62 grams of iodobenzene, and to the clear solution 16 grams of anhydrous cupric sulphate were added. The mixture was then boiled for three hours under reflux, cooled, decomposed with ice, and the solution obtained after acidifying extracted with ether, and so on. Sixteen grams of pure diphenyl were isolated, corresponding with a 66 per cent. yield on the iodobenzene used.

OBITUARY NOTICE.

EDWARD FRANK HARRISON.

BORN JULY, 1869; DIED NOVEMBER 4TH, 1917.

EDWARD FRANK HARRISON was educated at the United Westminster Schools, and in 1884 was apprenticed to a pharmaceutical chemist in North London. In 1890 he gained the Bell scholarship of the Pharmaceutical Society, and proceeded to its school in Bloomsbury Square. There he was awarded medals and certificates in chemistry, botany, and materia medica, and after passing the minor and major examinations he occupied several positions on the staff, and carried out research on the alkaloids of aconite. While acting afterwards for five years with the firm of Messrs. Brady and Martin at Newcastle, he successfully used his leisure to prepare for the B.Sc. degree of London University. The next six years were spent as head of the analytical department of Messrs. Burroughs Wellcome and Co. In 1905 he went into partnership in a school of pharmacy, but finally took up the independent practice of consulting and analytical chemistry. He was an eminent specialist in the analysis of drugs and medicinal substances, and as analyst to the British Medical Association made nearly all the analyses of proprietary articles which were revealed in the two publications "Secret Remedies" and "More Secret Remedies."

In the Parliamentary inquiry which followed these disclosures, Harrison was a most important witness and made a deep impression on the Select Committee. The full value of this work to public health and public economy has yet to be realised.

Col. Harrison was a Fellow of the Institute of Chemistry, and published a number of papers on his special province of the science. His process for estimating the diastatic strength of malts is now in general use. He was active both as a student and a past student in the life of the Pharmaceutical Society's School, in which he was most highly regarded, and to which as his *alma mater* he was loyally devoted. He was a member of the board of examiners, and in 1917 he delivered a thoughtful and valuable address at the inauguration of the session. For three years he conducted the practical chemistry competitions maintained in the weekly

Pharmaceutical Journal. His professional life was, indeed, in the highest degree strenuous.

As soon as the War broke out Harrison was impatient to join the forces. After being refused several times on the ground of age, he became a special constable and a volunteer in the Inns of Court Reserve Corps. Later he succeeded in entering as a private in the Sportsmen's Battalion of the Royal Fusiliers. It was by an accident that he came under the notice of the first head of the anti-gas service at home, Col. Sir W. H. Horrocks, R.A.M.C., who with some difficulty succeeded in securing his services. He was given the rank of lieutenant on the general list in July, 1915, and from that time devoted himself to the anti-gas service. It was only in the last year that his duties extended over both branches of the gas service.

He was promoted major in April, 1916; lieutenant-col. in January, 1917. He was appointed Assistant Controller of Chemical Warfare in November, 1917; shortly before his death, his succession to Major-General Thuillier as Controller of Chemical Warfare had been settled, and in a few days he would have attained the rank of brigadier-general.

Harrison's work for the war may be considered as falling into two periods. In the first period, extending from the spring of 1915 until November of 1916, he was engaged in research work in the anti-gas laboratories at the Royal Army Medical College, Millbank, the chief subjects being the improvement of the anti-gas helmet, the devising of, first, the large, and then the small box respirator.

In the early part of this period Harrison was constantly in the laboratory, working late into the night. He realised from the first the critical importance of speed and the possession of the initiative, and up to the last he never relaxed the pace. It is not easy to give an idea of the range of problems, their variety and complexity, that had to be overcome in bringing to a state of service efficiency such simple-looking appliances as the helmet and box respirator. The mechanical, chemical, physiological, and, one may add, even psychological questions raised were innumerable. Many heads and hands contributed to achieve the success that ensued. The apportionment of credit does not arise here, but there can be little doubt that all concerned would agree in giving Harrison a foremost place. With his scientific knowledge were united a strong practical instinct and intuitive judgment, which enabled him to seize quickly the essence of a problem and the substance of a suggestion, and to preserve a splendid sense of proportion. He improved the formula for the impregnating fluid

of the helmet, and worked out laboratory tests for controlling its component materials and for testing its efficiency. He made numerous experiments, in which he fearlessly wore the helmet in gases for which suitable quantitative control tests had not then been devised. During the late summer and autumn of 1915, he was occupied chiefly in getting out the large box respirator. As is generally known, this appliance was based on the admirable suggestion by Bertram Lambert, of Oxford, of a filter of permanganate-soda-lime granules. The realisation of this plan in the form of a box which in itself and its contents should be serviceable under field conditions was a most difficult undertaking. By the end of the year it was completed, and an issue was made early in 1916. The production in large quantities at a time when a high grade of protection was becoming indispensable for troops in special situations was a great achievement, and the large box was in its chief essentials the prototype of the small box which not long after became and remained the standard protection for troops of all arms. For the design of the small box, the members of the Gas Service in France were able to make valuable suggestions based on field experience with the large box. Harrison also made many contributions based on his own practical trials.

During the second period of his work, Harrison was closely associated with Col. Sir W. H. Horrocks in the rapid organisation and development of factories for the manufacture of respirators. Though this withdrew him for the greater part of his time from the laboratory, he remained in close touch with it, and at the weekly meeting of senior officers his genius for improvisation, his sound chemical judgment, and his foresight as to profitable lines of work were constantly evident. It was at this period that the manufacture of a new type of granule and of absorptive charcoal was worked out in the laboratories and transferred under the direction of selected officers to manufacturing establishments. In the choice of officers, Harrison's judgment rarely led him astray, and his knack of getting the right men into the right place contributed largely to the success of all his work. The great success of the small box respirator and its remarkable freedom from faults were due in no small measure to the organisation of inspecting officers, on which Harrison laid great stress. Harrison was held in high esteem by the officers of the Gas Services of our French, Italian, and American Allies. He was received with great cordiality at their councils, and his opinion was eagerly sought. It may be remarked, as affording a tribute to the excellence of the British respirator, that the Italians were supplied with several millions, and that the Americans, besides taking large numbers,

paid us the compliment of copying it as soon as the home manufacture could be arranged. The French considered that the protection it gave was even unnecessarily high.

In the last year of his life Harrison was called on to participate in the offensive side of gas warfare, and to exercise his great organising talent in what had become a very imposing and difficult undertaking. He had now reached the position to which his talents and labours so justly entitled him, but before he could actually officiate as Director of Chemical Warfare, the haunting fear of his friends was realised, and he was prostrated by influenza. His bodily strength, sapped by unceasing labour, was unequal to the strain, pneumonia supervened, and he passed away, as certainly as anyone on the battlefield, a sacrifice of the war. His elder son had fallen in France in 1916.

It is not easy to do justice to Harrison's personal qualities. He was a man of the strongest character. The love of his country, its ideals of freedom, its democratic institutions, and his belief in the destiny of the British as leaders among free peoples were the inspiration of his life and work. He had no thought for himself when the lives of others were at stake. The inflexible sense of duty which animated him communicated itself to those who worked with him, and he gained in a remarkable degree their respect and affection. He faced all emergencies with imperturbability, was never daunted or discouraged, and preserved a clear head and a power of decision even when worn out with incessant labour. He was neither dogmatic nor impatient, but always ready to improve on himself, listening with patience and courtesy to all honest criticism or advice. He was a master organiser, and the War brought him his opportunity. He died acknowledged and revered as a leader of men, his great task accomplished. He was buried with full military honours, mourned by a multitude of fellow-labourers who had learned something of his worth.

Harrison died before he had received the public honours that would undoubtedly have been conferred on him. He had been made C.M.G. in 1917, and the French had shown their appreciation of his services by making him Officer of the Legion of Honour. It is gratifying to know that a memorial to perpetuate his name is to be associated with the Chemical Society. What the nation owes him for the saving of life and the mitigation of suffering can scarcely be overestimated.

A. S.

H. S. R.

Organic Chemistry.

Graphic System of Representing Hydrocarbons. W.A. OSTWALD (*Chem. Zeit.*, 1919, **43**, 121—122).—If the percentage and relative proportional composition of hydrocarbons be graphically represented in a system in which the ratios of the percentages of hydrogen and carbon form the ordinates and the ratios of the number of atoms of hydrogen to carbon form the abscissæ, the connected points of intersection form a straight line terminated at one end by methane and at the other by pure carbon. On this line there are two well-marked points, that occupied by the olefines with the ratio of $H:C=2:1$ and the ratio of the percentages of $H:C=0.167$, and that occupied by benzene and acetylene with $H:C=1:1$ and $\%H:\%C=0.083$. The first point is approached by the paraffins, starting from methane, whilst the second point forms the starting place for the series of aromatic and acetylene hydrocarbons with increasing molecular weight (in the upward direction towards the olefine point), and also for the hydrocarbons rich in carbon and with many rings in their structure (in the downward direction leading towards pure carbon). By dropping as perpendiculars on to the line the molecular weights, a co-ordinated system is obtained in which, in the case of homologous series, the atoms of carbon as lines cut the atoms of hydrogen as curves. Analogous representations are obtained when the percentage of hydrogen and atoms of hydrogen, the percentage of carbon and atoms of carbon, the percentage of hydrogen and atoms of carbon, and the percentage of carbon and atoms of hydrogen are chosen as co-ordinates. For example, in a graphic representation on the last-named system, benzene, naphthalene, and anthracene lie on one curve, the continuation of which leads to chrysene, picene, and other hydrocarbons of multi-ringed structure. In the whole field, homologous series fall together in lines which show recognised chemical relationships.

C. A. M.

Production of Ethyl Alcohol from Algæ. ED. KAYSER (*Ann. Chim. anal.*, 1919, [ii], **1**, 79—80).—The marine algæ *Laminaria leucocaulis* and *L. saccharina*, when heated with water under pressure, yield a liquid which ferments readily; about 3.7 litres of alcohol are obtained per 100 kilos. of dry algæ. If the digestion is made with 7% sulphuric acid and the liquid obtained nearly neutralised before fermentation, the yield of alcohol may be increased to about 12 litres. [See, further, *J. Soc. Chem. Ind.*, 1919, 266A.]

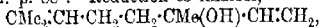
W. P. S.

Synthesis of Linalool. L. RUZICKA and V. FORNASIR (*Helv. Chim. Acta*, 1919, **2**, 182—188).—Tiemann and Semmler's formula for linalool has now been confirmed by synthesis. Methylhepten-

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one (from citral; Verley, A., 1898, i, 557) is dissolved in ether, mixed with finely powdered sodamide, and then submitted to a slow current of acetylene at a low temperature, when a good yield of *dehydrolinool*, $\text{CMe}_2\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}(\text{OH})\cdot\text{C}\equiv\text{CH}$, is obtained. This is a colourless, mobile oil, b. p. 91—93°/12 mm., D^{15}_4 0.8855, with an odour like citral, and it forms a *phenyl-carbamate*, m. p. 88°. Reduction to linalool,



is effected by shaking an ethereal solution of the oil with thin shavings of sodium (8 atomic proportions) applied in four separate portions, a few drops of water being added from time to time.

J. C. W.

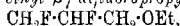
Spontaneous Inflammation of Mixtures of Air and Ethyl Ether Vapour. E. ALLAIRE (*Compt. rend.*, 1919, 168, 729—730).

—Under the experimental conditions, it was found that spontaneous inflammation of a mixture of air and ethyl ether vapour occurred at about 190°, when the amount of ether in the gaseous mixture was 1 gram per litre. No reaction took place at the ordinary temperature.

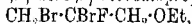
W. G.

Ethyl Fluorobromopropyl Ether and Ethyl Fluoroallyl Ether. FRÉD. SWARTS (*Bull. Soc. chim.*, 1919, [iv], 25, 103—107).

—Ethyl allyl ether when brominated yields *ethyl dibromopropyl ether*, $\text{CH}_2\text{Br}\cdot\text{CHBr}\cdot\text{CH}_2\cdot\text{OEt}$, b. p. 103.5°/35 mm., which when heated with mercurous fluoride or silver fluoride gives ethyl bromide and a certain amount of *ethyl β-fluoro-γ-bromopropyl ether*, $\text{CH}_2\text{Br}\cdot\text{CHF}\cdot\text{CH}_2\cdot\text{OEt}$, b. p. 156.4—157.3°, D^{16}_4 1.484, together with a little *ethyl β-γ-difluoropropyl ether*



b. p. 114.5°. When heated with sodium methoxide in methyl-alcoholic solution, ethyl fluorobromopropyl ether yields *ethyl β-fluoroallyl ether*, $\text{CH}_2\text{F}\cdot\text{CH}_2\cdot\text{OEt}$, b. p. 77.5°, $D^{15.1}_4$ 0.91659, n_D 1.37665, n_D 1.3790, n_D 1.38874, which readily combines with bromine, giving *ethyl β-fluoro-β-γ-dibromopropyl ether*,



b. p. 188°.

W. G.

Action of Alkyl Iodides on Normal Sodium Phosphate in Aqueous Solution. OCTAVE BAILLY (*Compt. rend.*, 1919, 168, 560—563).

—The lower members of the series of alkyl iodides react with normal sodium phosphate in aqueous solution when heated in sealed tubes at 60° or 100°, giving the disodium alkyl phosphates and a small amount of the monosodium dialkyl phosphates. The yield diminishes rapidly from 73.5% in the case of methyl iodide to 10.6% in the case of *isobutyl* iodide as the molecular weight increases. The following normal alkali and alkali-earth salts of the alkyl phosphates have been prepared: *strontium*, *potassium*, *ammonium*, and *sodium methyl phosphates*; *strontium* and *sodium ethyl phosphates*; *calcium* and *strontium propyl phosphates*;

calcium, strontium, and sodium isopropyl phosphates; calcium and strontium isobutyl phosphates; strontium allyl phosphate. The solubility of the alkali-earth alkyl phosphates diminishes from the barium salts through the strontium salts to the calcium salts, which are almost insoluble.

W. G.

Formic Acid is as much an Aldehyde. MAURICE PRUD'HOMME (*J. Chim. Phys.*, 1918, **16**, 438—441).—From a study of the heats of formation and combustion of formic acid, the author concludes that, under the conditions of temperature and pressure prevailing when combustion occurs, formic acid behaves as a mixture of equal parts of the tautomeric acid and hydroxy-aldehyde forms.

W. G.

Nature of the Fatty Acids produced by the Oxidation of Brown Coal Tar Oil. C. HARRIES (*Ber.*, 1919, **52**, [B], 65—72).—The fatty acids produced by treating brown coal-tar oil (freed from solid paraffins and phenols, and then having b. p. 125—220°/10 mm.) with ozone and decomposing the resulting ozonides (Harries, Koetschau, and Fonrobert, *Chem. Zeit.*, 1917, **16**, 117) have been esterified by Fischer's method; and the esters separated by fractional distillation. Formic, acetic, propionic, oxalic, palmitic, stearic, and myristic acids have been identified, and two other acids, probably heptic and octic acids, isolated. The complete absence of the fatty acids $C_4H_8O_2$ — $C_6H_{12}O_2$ is remarkable.

C. S.

Preparation of certain Organic Salts of Tellurium.

AARON M. HAGEMAN (*J. Amer. Chem. Soc.*, 1919, **41**, 342—346).—Tellurium hydrogen tartrate is formed by heating at 70° tellurium dioxide with a solution of tartaric acid for several months. The solution may not be boiled, for a quantity of tellurium is thereby separated. Since the tartrate cannot be separated from tartaric acid by crystallisation, it is necessary to use the exact quantities required in the preparation. The pure salt has the formula $Te(HC_4H_4O_6)_4$. Tellurium hydrogen citrate, $Te(HC_6H_5O_7)_2$, is formed as a white, opaque, crystalline compound which separates in radiating clusters. It is produced by boiling tellurium dioxide with an aqueous solution of citric acid for a month. This compound does not deposit tellurium on boiling, and may be separated from citric acid by crystallisation. Succinic acid does not attack tellurium dioxide. Solutions of oxalic, lactic, malic, and gallic acids hold appreciable quantities of tellurium dioxide in solution, but it was found impossible to separate a crystalline compound of tellurium with any of these acids from solution. It is possible that an oleate and stearate of tellurium exist, but a pure, crystalline compound could not be obtained by the action of tellurium tetrachloride in benzene on a benzene solution of copper oleate or stearate.

J. F. S.

Polymerisation of Formaldehyde by Alkalis. C. MANNICH (*Ber.*, 1919, **52**, [B], 160—162).—By keeping 30% formaldehyde solution (almost free from methyl alcohol) containing 1—4% of anhydrous sodium carbonate, 0.3% of sodium hydroxide or 0.3% of calcium oxide for four months, crystals, the separation of which begins within one day, are obtained, which prove to be α -poly-oxymethylene (Auerbach and Barschall, A., 1908, i, 131). The yield, which is 43% of the theoretical in the best case (with 4% of sodium carbonate), is diminished if methyl or ethyl alcohol is present. C. S.

Improvements in the Manufacture of Diethyl and Dimethyl Ketones. NEVIL VINCENT SIDGWICK and BERTRAM LAMBERT (Brit. Pat., 14085 of 1915).—A practically quantitative yield of acetone or of diethyl ketone may be obtained by passing the vapour of acetic or propionic acid over manganous oxide at 350°. The process may be carried out either with or without the dilution of the acid with water, and an acid diluted to 20% may be used. The catalyst is prepared by boiling pumice stone in a strong aqueous solution or suspension of manganous acetate or carbonate, and continuing the boiling until all the water is evaporated, the temperature not being allowed to rise above 200° unless air is excluded. W. G.

Action of Neutral Salts on the Inversion of Sucrose by Acids. H. COLIN and M. LEBERT (*Bull. Assoc. Chim. Sucr. Dist.*, 1918, **35**, 14—17).—A study of the inhibitive influence of sodium acetate, sodium citrate, and potassium oxalate on the hydrolytic action of the respective acids and on that of hydrochloric acid. The results are in accord with the known retrogression of the degree of electrolytic dissociation of weak acids in presence of their salts. [See *J. Soc. Chem. Ind.*, 1919, May.] J. H. L.

Transformations of Nitrocellulose. A. ANGELI (*Atti R. Accad. Lincei*, 1919, [v], **28**, i, 20—24).—Nitrocellulose in the form of collodion cotton or guncotton is readily gelatinised by pyridine (compare Walter, A., 1911, i, 124), a large proportion of the latter yielding dense liquids which have the appearance of collodion, and gradually diminish in viscosity until, after a few days at the ordinary temperature, they resemble in this respect the pure pyridine; this phenomenon serves to detect unaltered cellulose in nitrocellulose. Treatment of the collodion cotton with just sufficient pyridine to moisten it yields a semi-solid, transparent mass with the appearance of caoutchouc, this also becoming continually more fluid until it is able to pass through filter paper. The yellow liquid thus formed smells strongly of pyridine, and with water gives an almost white mass, which has a resinous appearance and tenaciously retains pyridine. When freed from the latter by means of alcohol and dilute sulphuric acid, reprecipitated, washed, and dried over sulphuric acid, the product forms a white, amorphous powder, soluble readily in acetone and to a less extent

in alcohol, and almost insoluble in ether or benzene; the yield is about 80% of the collodion cotton used. The compound contains 9—10% of nitrogen, and somewhat resembles the substance obtained in small proportion by Berl and Fodor (A., 1911, i, 264) by treatment of very dilute alcoholic or ethereal solution of nitrocellulose with alkali hydroxide or sodium carbonate. It begins to turn brown at about 165°, and becomes almost black at 250°. When its alcoholic solution is poured into water, it forms a very stable, opalescent, colloidal solution, which is coagulated immediately by sodium chloride, ammonium sulphate, or gelatin solution, but is not precipitated by aqueous tannin solution. With benzene and sulphuric acid, it gives nitrobenzene, and with sulphuric acid in presence of mercury, nitric oxide. On a wet dimethylaminoazobenzene paper, it forms slowly an intensely red spot. It reduces ammoniacal silver nitrate and reacts readily with phenylhydrazine, but has no action on Fehling's solution. Quinoline and nicotine also act, but more slowly, on nitrocellulose.

T. H. P.

Origin of Creatine. III. KARL THOMAS and M. G. H. GOERNE (*Zeitsch. physiol. Chem.*, 1919, 104, 73—87. Compare A., 1914, i, 353, 1110).—No increase in the urinary creatine was observed to follow the oral or subcutaneous administration of ϵ -methylguanidinohexic acid or γ -methylguanidinobutyric acid to rabbits. The preparation of these acids and certain closely related compounds is described. *Toluenesulphonyl- ϵ -amino-*n*-hexoic acid*, $C_6H_5Me \cdot SO_2 \cdot NH \cdot [CH_2]_5 \cdot CO_2H$, crystallises from water in slender needles, m. p. 104—106°. *Toluenesulphonyl- ϵ -methylamino-*n*-hexoic acid*, $C_6H_5Me \cdot SO_2 \cdot NMe \cdot [CH_2]_5 \cdot CO_2H$, crystallises from water or ethyl acetate in white, slender needles, m. p. 55—59°. *ϵ -Methylamino-*n*-hexoic acid*, $NHMe \cdot [CH_2]_5 \cdot CO_2H$, crystallises with 1½ molecules of water. The hydrated form melts indefinitely at 67°; the anhydrous form, crystallised from alcohol, melts at 132°. *ϵ -Methylguanidinohexoic acid*, $NH_2 \cdot C(NH) \cdot NMe \cdot [CH_2]_5 \cdot CO_2H$, prepared from ϵ -methylamino-*n*-hexoic acid (ϵ -methyl-leucine) and cyanamide, crystallises with difficulty from water in microscopic tufts of needles. It decomposes without melting about 285°. The hydrochloride of this acid crystallises from alcohol in slender needles, m. p. 105°, and the nitrate melts indefinitely at 80—85°. For purposes of identification, the acid oxalate serves best. This salt crystallises from water in needles, m. p. 167—168° (uncorr.). *Methylcarbamido-*n*-hexoic acid*, $NH_2 \cdot CO \cdot NMe \cdot [CH_2]_5 \cdot CO_2H$, crystallises from water in stout needles, m. p. 163° (decomp.). *Toluenesulphonyl- γ -aminobutyric acid*, $C_6H_5Me \cdot SO_2 \cdot NH \cdot [CH_2]_3 \cdot CO_2H$, m. p. 135°, crystallises from water. *Toluenesulphonyl- γ -methylaminobutyric acid*, $C_6H_5Me \cdot SO_2 \cdot NMe \cdot [CH_2]_3 \cdot CO_2H$, m. p. 96—98°, crystallises from dilute alcohol. γ -Methylaminobutyric acid is very hygroscopic. *γ -Methylguanidinobutyric acid*, $NH_2 \cdot C(NH) \cdot NMe \cdot [CH_2]_3 \cdot CO_2H$.

was not obtained in the pure condition. *γ*-Carbamidobutyric acid, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot(\text{CH}_2)_3\cdot\text{CO}_2\text{H}$, m. p. 175–176° (decomp.), crystallises from water or alcohol. J. C. D.

Bromination of Unsaturated Compounds with *N*-Bromoacetamide. The Law of the Course of Chemical Reactions.

A. WOHL (*Ber.*, 1919, 52, [B], 51–63).—In the presence of cold acetone or ethyl ether as solvent, acetobromoamide reacts with certain substances as a brominating agent, acetamide being produced, but not hydrogen bromide. Thus *tert*.-butyl bromide is converted into *isobutylene* dibromide, phenol into *p*-bromophenol, anisole into *p*-bromoanisole, ethyl acetoacetate into ethyl α -bromoacetoacetate, and the half-amide of malonic ester into the half-amide of bromomalonic ester. β - γ -Dimethyl- Δ^2 -butene yields α -bromo- β - γ -dimethyl- Δ^2 -butene amongst other products. β -Methyl- Δ^2 -butene in ethereal solution yields dibrominated and more highly brominated products, but in acetone solution with 2 mols. of acetobromoamide it yields an unsaturated dibromo-derivative. In acetone solution, γ -bromo- β -methyl- Δ^2 -butene can be further brominated by acetobromoamide, and yields an unsaturated dibrominated product.

In the reactions between acetobromoamide and the preceding unsaturated compounds, there is no addition of fragments of the acetobromoamide molecule at the double linking, but the whole molecule must become attached to one of the carbon atoms by residual affinity; an interchange of hydrogen and bromine occurs between the two molecules, and acetamide and a bromine-substituted derivative of the unsaturated compound are produced.

C. S.

Mercury Fulminate and some of its Impurities.

PAUL NICOLARDOT and JEAN BOUDET (*Bull. Soc. chim.*, 1919, [iv], 25, 119–122).—Sodium and ammonium thiosulphates in 5% aqueous solutions are much more satisfactory solvents than potassium cyanide at the same concentration for analytical purposes, since they do not dissolve the impurities likely to be present in the fulminate, whilst these are soluble in the potassium cyanide solution. Heaven's method (*A.*, 1918, ii, 233) for the estimation of mercury fulminate, may be applied to the extract made with either of the thiosulphates. For the method of recovery of mercury from the residues in the manufacture of mercury fulminate, see *J. Soc. Chem. Ind.*, 1919, May.

W. G.

Organic Fluorine Compounds. III.

I. J. RINKES (*Chem. Weekblad*, 1919, 16, 206–213).—The assertion of Meyer and Hub (*A.*, 1910, i, 735) that by means of the Hoffmann reaction no fluoroaniline is obtained from *o*-fluorobenzamide is disproved, the reaction being, on the contrary, an excellent preparative method giving good yields of fluoroaniline. *o*-Fluorobenzamide was prepared from *o*-toluidine by diazotising in presence of hydrofluoric

acid. The oxidation of the *o*-fluorotoluene is effected by the chlorination of the methyl group and subsequent hydrolysis, which permits of the preparation of the aldehyde. This method is preferable to the direct oxidation by means of permanganate. *p*-Fluorobenzaldehyde was prepared in a similar way, and with hydroxylamine hydrochloride and sodium carbonate gives directly *p*-fluoroantialdoxime (m. p. 81.2°). Regeneration of the oxime from the hydrochloride by means of sodium carbonate gives *p*-fluorosynaldoxime (m. p. $116-117^{\circ}$). *o*-Fluorobenzaldoxime hydrochloride on treatment with sodium carbonate yields the original antialdoxime. This behaviour is analogous to that of *o*- and *p*-chlorobenzaldoximes.

o-Fluoriodobenzene, b. p. $188.6^{\circ}/759$ mm., was prepared from *o*-fluoroaniline by diazotising and adding potassium iodide.

p-Fluoriodobenzene, b. p. $183.2^{\circ}/760$ mm., was prepared in a similar way. This was obtained in two crystalline forms, m. p. -27.2° and -18° respectively.

An attempt to prepare fluorine derivatives of iodobenzene with fluorine in the nucleus was unsuccessful. Phenyl iododifluoride was first prepared from iodosobenzene and fuming hydrofluoric acid. This was kept for three months in a copper tube. No formation of fluoroiodobenzene was observed, the principal product being apparently diphenyl.

p-Fluoronitrosobenzene was prepared from *p*-fluoroaniline by oxidation by means of ammonium persulphate, and its behaviour studied with respect to condensation in concentrated sulphuric acid. The chief condensation product was found to be 2:7-difluorophenine-5:10-oxide, brownish-yellow needles, m. p. 150° , analogous to the corresponding chlorine derivative obtained by Bamberger and Jan (A., 1911, i, 684).

W. S. M.

Catalytic Dehydrogenation by Nickel in the Presence of Hydrogen.

PAUL SABATIER and GEORGES GAUDION (*Compt. rend.*, 1919, 168, 670—672).—Hydrocarbons of the benzene series when passed with hydrogen over nickel at 180° undergo hydrogenation, but if the temperature is raised to $350-360^{\circ}$, dehydrogenation occurs. Thus at this higher temperature pinene yields a mixture of cymene and cumene; limonene and camphene yield the same mixture; menthene gives cymene; cyclohexene gives benzene; cyclohexanol gives phenol; pulegone gives a mixture of cresol and thymol; eucalyptol, terpene, and terpineol undergo dehydration as well as dehydrogenation. The presence of hydrogen is essential for this dehydrogenation.

W. G.

Formation and Stability of spiro-Compounds. II. Bridged-spiro-compounds Derived from cyclo-Hexane. CHRISTOPHER KELK INGOLD and JOCELYN FIELD THORPE (T., 1919, 115, 280—333).

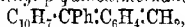
Solubilities, Separation, and Purification of Anthracene, Carbazole, and Phenanthrene. JOHN MARSHALL CLARK (*J. Ind. Eng. Chem.*, 1919, 11, 204—209).—Various solvents have been proposed for separating anthracene, carbazole, and phenanthrene from the "anthracene oil" of coal tar, but none effects complete separation, and chemical methods are required to complete the purification. At 15.5°, benzene dissolves 1.04% of anthracene, 0.72% of carbazole, and 16.72% of phenanthrene; acetone dissolves 0.55% of anthracene, 6.12% of carbazole, and 15.08% of phenanthrene; and light pyridine, 0.83%, 12.45%, and 25.54% of the respective substances. In the method described, crude coal-tar solvent naphtha is used to remove the phenanthrene, and pyridine to separate carbazole from anthracene. The anthracene is then purified by fusion with alkali, to retain the carbazole and sublimation, whilst carbazole is purified by treatment with 98% sulphuric acid, which combines with anthracene to form a sulphonated compound soluble in a large volume of water, whilst the carbazole is scarcely affected. In the fusion with alkali, the best results are obtained by the use of a mixture of potassium and sodium hydroxides. [See further, *J. Soc. Chem. Ind.*, 1919, 247A.] C. A. M.

***p*-Quinodimethanes.** W. SCHLENK and EGON MEYER (*Ber.*, 1919, 52, [B], 8—21).—*as*-Diaryl-*p*-quinodimethanes,

$$\text{C}_6\text{Ar}_2\text{C}_6\text{H}_4\text{CH}_2$$

have now been prepared, essentially by Tschitschibabin's method (A., 1908, i, 872), but in some cases the product is difficult (or impossible) to isolate on account of its tendency to polymerise. Thus, *as*-diphenyl-, *as*-phenyl-*p*-tolyl-, and *as*-phenyldiphenyl-quinodimethanes could not be isolated, and *as*-di- α -naphthylquinodimethane could only be obtained in solution.

By keeping at the ordinary temperature, or more rapidly by warming, a solution of phenyl-*p*-tolyl- α -naphthylchloromethane in pyridine with the complete exclusion of air and in the absence of light, *as*-phenyl- α -naphthyl-*p*-quinodimethane,



is obtained. Its isolation is difficult, but the substance is ultimately obtained as a dark blue powder. Its solutions are intensely bluish-violet, and in the dilute state exhibit a green fluorescence. Its ethereal solution is instantly decolorised by oxygen, chlorine, bromine, or ferric chloride. The tendency to polymerise is relatively small, but it does polymerise, frequently without obvious cause.

In a similar manner, phenyl-*o*-tolyl-*p*-tolylchloromethane yields *as*-phenyl-*o*-tolyl-*p*-quinodimethane, $\text{C}_6\text{H}_7\text{CPhC}_6\text{H}_4\text{CH}_2$, violet powder, which is somewhat more stable than the preceding compound towards oxygen.

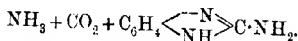
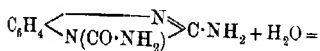
The intense colour of these two diarylquinodimethanes in comparison with that of tetra-arylquinodimethanes is very remarkable; also in solution they exhibit selective absorption in the visible

spectrum, whereas the tetra-aryl compounds show continuous absorption.

Phenyl-p-tolyl-α-naphthylcarbinol, $C_{10}H_7 \cdot CPh(C_7H_7) \cdot OH$, prepared in the usual way from magnesium α-naphthyl bromide and phenyl *p*-tolyl ketone, is a colourless, crystalline powder, m. p. 109–110°, which is converted by hydrogen chloride in ethereal solution into *phenyl-p-tolyl-α-naphthylchloromethane*, m. p. 142–144°. *Phenyl-o-tolyl-p-tolylchloromethane*, prepared in a similar manner, has m. p. 86.5°. *Phenyl-o-tolyl-diphenylcarbinol*, colourless crystals, m. p. 137–138°, and the *chloride*, $C_6H_5Ph \cdot CPhCl \cdot C_7H_7$, m. p. 161°, are described. *p-Tolyl-di-α-naphthylcarbinol* could not be isolated in a pure state, since by repeated crystallisation it is changed to *p-tolyl-di-α-naphthylfluorene*, $C_{10}H_6 > C(OH) \cdot C_7H_7$, needles, m. p. 162.5–163°.

C. S.

***o*-Aminophenylcarbamide.** GUIDO PELLIZZARI (*Gazzetta*, 1919, 49, i, 16–26).—This compound, prepared by a method simpler than that used by Schiff and Ostrogovich (*A.*, 1897, i, 144) for its meta- and para-isomerides, has basic properties, and treatment of its hydrochloride with potassium cyanate yields *o*-phenylenediamide. At 150°, it loses quantitatively 1 mol. of ammonia, giving *o*-phenylenecarbamide, which is prepared most simply in this way. Treatment of *o*-phenylenediamine with cyanogen bromide yields *o*-phenyleneguanidine, but in the case of *o*-aminophenylcarbamide, this reagent gives first *o*-cyanoaminophenylcarbamide, which is an acid compound stable in dry air, but is gradually changed by moist air or by water into the metameric basic compound, *o*-phenylene-α-guanylcabamide. The latter cannot be obtained pure in the free state, since it is hygroscopic and tends to undergo hydrolysis into *o*-phenyleneguanidine, ammonia, and carbon dioxide:



This decomposition, which occurs slowly in the cold and more rapidly in the hot, is greatly accelerated by the presence of either alkali or mineral acid. Thus the salts of *o*-phenylene-α-guanylcabamide could not, in general, be prepared, although the action of picric acid on cold aqueous *o*-cyanoaminophenylcarbamide yields the picrate, which is decomposed similarly by hot water. *o*-phenyleneguanidine picrate crystallising out from the solution.

The existence of this highly unstable *o*-phenylene-α-guanylcabamide confirms the constitutional formulæ attributed to the two *γ*-anoderivatives described previously (this vol., i, 134).

o-Aminophenylcarbamide, $\text{NH}_2 \cdot C_6H_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$, prepared by the action of potassium cyanate (1 mol.) on *o*-phenylenediamine

k*

monohydrochloride (1 mol.), forms shining needles, and shows signs of melting at 175° , then becomes opaque, and melts at 307° ; in a moist atmosphere, it has m. p. 175° (decomp.), a solid residue, m. p. 307° , which is that of *o*-phenylenecarbamide, remaining. Its *picrate*, $C_7H_5ON_3 \cdot C_6H_5O_2N_3$, forms an almost gelatinous, felted mass of long, very slender needles, decomposing at $200-235^{\circ}$. The *nitrate*, $C_7H_5ON_3 \cdot HNO_3 \cdot \frac{1}{2}H_2O$, long, white needles, reddens at $170-175^{\circ}$, and then contracts and undergoes gradual alteration. The hydrochloride and platinichloride crystallise well and are moderately soluble.

o-Cyanaminophenylcarbamide, $CN \cdot NH \cdot C_6H_4 \cdot NH \cdot CO \cdot NH_2$, forms small, white, shining crystals, and decomposes at 110° .

o-Phenylenecarbonylcarbamide *picrate*, $C_6H_5ON_3 \cdot C_6H_5O_2N_3$, forms a yellow powder and decomposes at $250-260^{\circ}$. T. H. P.

Compounds of Phenols, Phenolic Ethers, and Salicylaldehyde with Normal Salts. R. F. WEINLAND and GUSTAV BÄRLOCHER (*Ber.*, 1919, 52, [B], 147-159).—An extension of the work of Weinland and Denzel (A., 1914, i, 953; 1915, i, 526). *Compounds* of the type $CaX_2 \cdot 4C_6H_4(OH)_2 \cdot 2R \cdot OH$ have been obtained, where X is Cl, Br or I, and R is Me, Et, Prⁿ, or C_6H_{11} , from solutions of catechol and the calcium haloid (anhydrous) in the respective alcohols; they all form colourless crystals which are stable over sulphuric acid. Quinol forms similar compounds, but less readily, whilst resorcinol does not.

Quinol forms *compounds*, colourless crystals, with potassium formate, acetate, and propionate, $H \cdot CO_2K \cdot 2C_6H_4(OH)_2$, $2CH_3 \cdot CO_2K \cdot 3C_6H_4(OH)_2$,

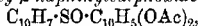
and $C_2H_5 \cdot CO_2K \cdot 2C_6H_4(OH)_2$. Pyrogallol forms *compounds*, $KA \cdot C_6H_3(OH)_3$, with the same three salts, whilst phloroglucinol forms the compound $CH_3 \cdot CO_2K \cdot C_6H_3(OH)_3$. All these compounds crystallise from alcoholic solutions of the components.

Compounds, colourless, stable crystals, have been obtained from guaiacol (2 mols.) and potassium formate, acetate, propionate or butyrate (1 mol.), guaiacol (2 mols.) and sodium acetate (1 mol.), eugenol (2 mols.) and potassium propionate (1 mol.), vanillin (1 mol.) and potassium propionate (1 mol.), vanillin (3 mols.) and potassium acetate, propionate or butyrate (2 mols.), and vanillin (2 mols.) and potassium formate or sodium acetate (1 mol.).

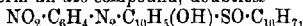
Compounds, pale yellow, stable needles, have been obtained from alcoholic solutions of salicylaldehyde (2 mols.) and potassium acetate, propionate or butyrate (1 mol.). C. S.

Derivatives of *iso*- α -Naphthyl-1:4-dihydroxy- β -naphthylsulphone. O. HINSBERG (*Ber.*, 1919, 52, [B], 28-35).—An instance of stereoisomerism analogous to that of the β -naphthol sulphides is described. α -Naphthyl-1:4-dihydroxy- β -naphthylsulphone (A., 1917, i, 575) undoubtedly belongs to the normal series of sulphones. By heating at 170° , it loses 1 mol. of water, and is converted into a *substance*, brownish-red, crystalline powder, sintering at 85° and

completely molten at 105° , which undoubtedly has the formula $C_{10}H_7 \cdot SO_2 \cdot C_{10}H_5O_2$, and, on account of its ready solubility, low and indefinite m. p., and intense colour, belongs to the *iso*-series, and is therefore *iso- α -naphthyl-2- α -naphthaquinonylsulphoxide* (two by-products are formed in this reaction, the one a grey, very sparingly soluble substance, the other, yellow crystals, m. p. 225° [decomp.]). The *iso*-sulphoxide is reduced and acetylated by zinc dust and acetic anhydride on the water-bath, yielding *iso- α -naphthyl-1:4-diacetoxy- β -naphthylsulphoxide*,



pale yellow, crystalline powder containing $\frac{1}{2}CHCl_3$ (from chloroform), decomp. 73° and completely molten at 105° . The *iso*-sulphoxide combines with *p*-nitrophenylhydrazine in warm glacial acetic acid to form an *azo*-compound, doubtless

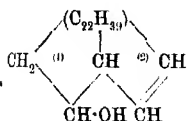


red powder, and is oxidised in warm glacial acetic acid solution by 30% hydrogen peroxide, yielding *iso- α -naphthyl-2- α -naphthaquinonylsulphone*, $C_{10}H_7 \cdot SO_2 \cdot C_{10}H_5O_2$, yellowish-brown needles or crusts containing $\frac{1}{2}H_2O$, m. p. $110-115^{\circ}$ (decomp.), which is quite different from the isomeric *α -naphthyl-2- α -naphthaquinonylsulphone* (*loc. cit.*), exhibits its quinone nature by reacting with aniline and with *p*-nitrophenylhydrazine, and is reduced and acetylated by zinc dust and acetic anhydride, yielding a colourless substance, probably *iso- α -naphthyl-1:4-diacetoxy- β -naphthylsulphone*.

C. S.

Cholesterol. XXVI. Ring Systems in Cholesterol. A.

WINDAUS and O. DALMER (*Ber.*, 1919, 52, [B], 162-169).—Investigations demonstrative of the number of atoms in the two ring systems of the cholesterol molecule (Windaus, A., 1917, i, 265) have not hitherto been undertaken. The authors attack the problem as follows. By hydrogenation at the double linking



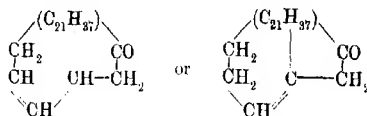
(annexed formula), ring 2 is rendered proof against oxidation, and ring 1 is then ruptured; if, on the other hand, the hydroxyl group in ring 1 is replaced by hydrogen, ring 2 is then ruptured on oxidation. In both cases, dicarboxylic acids are obtained, in which the positions

of the carboxyl groups are determined with great probability by Blanc's method with acetic anhydride (A., 1907, i, 710).

Dihydrocholesterol (β -cholestanol), obtained by reducing cholesterol in acetic acid solution at 100° with hydrogen and palladium, is oxidised to the dicarboxylic acid, $C_{27}H_{46}O_4$ (Windaus and Ubrigg, A., 1914, i, 1066). By heating with acetic anhydride until the reagent has distilled completely, and then at $250^{\circ}/15-20$ mm., this acid is converted into a *ketone*, $C_{26}H_{44}O$, leaflets, m. p. $100-100.5^{\circ}$ (*oxime*, needles, m. p. 203°), which is oxidised by glacial acetic and nitric (D 148) acids at $75-80^{\circ}$ to a dibasic acid, $C_{26}H_{44}O_4$, needles, m. p. $234-235^{\circ}$. This acid, by treatment

with acetic anhydride and subsequent heating in a vacuum, yields its *anhydride*, $C_{26}H_{42}O_3$, crystals, m. p. 153° . The carboxyl groups in this acid, therefore, are in the 1:5-positions, those in the acid $C_{27}H_{46}O_4$ are in the 1:6-positions, and ring 1 of the cholesterol molecule contains six atoms of carbon.

Cholestene did not prove a suitable material for the rupture of ring 2, since it did not yield the desired dicarboxylic acid on oxidation. Therefore α -chlorocholestanone in alcoholic solution was converted by 20% potassium hydroxide at 50° into *heterocholestenone*,



needles, m. p. 96° , which was reduced in glacial acetic acid solution by hydrogen and palladium to *heterocholestanone*, $C_{27}H_{46}O$, leaflets, m. p. $98-99^\circ$ (*oxime*, needles, m. p. 195°). The latter ketone, which can also be obtained by reducing nitrocholestene with zinc dust and acetic acid, and yields cholestane by reduction by Clemmensen's method, is converted by glacial acetic and nitric

(D. 1.48) acids at $70-75^\circ$ into a dibasic acid, $C_{27}H_{46}O_4$, needles, m. p. 273° (decomp.), which yields its *anhydride*, $C_{27}H_{44}O_3$, needles, m. p. 118° , by treatment with acetic anhydride and subsequent distillation in a vacuum. The carboxyl groups in the acid $C_{27}H_{46}O_4$, therefore, are in the 1:4- or 1:5-positions. Only the latter alternative is permissible, and ring 2 there-

fore contains five atoms of carbon. On the assumption, therefore, that Blanc's method gives trustworthy results in the case of complicated cyclic structures, the constitution of the cholesterol molecule has been elucidated to the extent indicated in the annexed formula.

C. S.

Cholesterol. XXVII. Isomerism of Cholestane and ψ -Cholestane. A. WINDAUS (*Ber.*, 1919, 52, [B], 170-176. Compare preceding abstract).—Cholestane is without doubt the normal dihydro-derivative of cholestene. ψ -Cholestene, which yields ψ -cholestane by reduction in ethereal solution by hydrogen and platinum (Mauthner, A., 1907, i, 921; 1909, i, 714), is now found to give cholestane almost exclusively when reduced in glacial acetic acid solution by hydrogen and palladium at 75° . Cholestene and ψ -cholestene, therefore, differ only in the position of the double linking. ψ -Cholestane can therefore very well be a diastereoisomeride of cholestane, ring 2 (*loc. cit.*) being affixed to ring 1 in the *cis*-position. Some experimental observations support the new formulation. Dihydrocholesterol, derived from cholestane, is con-

verted through the acid $C_{27}H_{46}O_4$ into the ketone $C_{26}H_{44}O$ (*loc. cit.*). Coprosterol, derived from ψ -cholestane, yields by oxidation the isomeric acid $C_{27}H_{46}O_4$, which by evaporation with acetic anhydride and subsequent distillation in a vacuum is converted into an isomeric ketone, $C_{26}H_{44}O$, needles, m. p. 73—74°. The very smooth course of the ketone formation indicates that the two carboxyl groups in the two isomeric acids are in the *cis*-position. The acid $C_{27}H_{44}O_4$ obtained from cholesterol by Diels and Abderhalden (A., 1904, i, 880) is reduced in glacial acetic acid solution at 100° by hydrogen and palladium to a third isomeric acid, $C_{27}H_{46}O_4$, leaflets, m. p. 252° (methyl ester, $C_{26}H_{50}O_4$, prisms, m. p. 123—124°), which is converted by the acetic anhydride method, although far less smoothly, into the ketone, $C_{26}H_{44}O$, obtained from coprosterol through the second isomeric acid $C_{27}H_{46}O_4$. It is extremely probable, therefore, that the two acids $C_{27}H_{46}O_4$ last mentioned only differ from one another in that the two carboxyl groups in the former (which is less readily converted into the ketone) are in the *trans*-position, and in the latter are in the *cis*-position.

C. S.

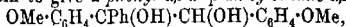
Molecular Transpositions of α -Glycols. II. Product of Dehydration of $\alpha\beta$ -Triphenylpropan- $\alpha\beta$ -diol. A. ORÉKHOFF (*Bull. Soc. chim.*, 1919, [iv], 25, 108—111. Compare this vol., i, 146).—Magnesium benzyl chloride condenses with benzoin to give $\alpha\beta$ -triphenylpropan- $\alpha\beta$ -diol, $CH_2Ph \cdot CPh(OH) \cdot CHPh(OH)$, m. p. 159—160°, giving a monoacetyl derivative, m. p. 176—177°. The glycol, when dehydrated with sulphuric acid, yields benzyl diphenylmethyl ketone, $CHPh_2 \cdot CO \cdot CH_2Ph$, m. p. 80—81°, giving an oxime, m. p. 134—135°, and a phenylhydrazone, m. p. 99—100°. This ketone, when heated with alcoholic potassium hydroxide, is decomposed, giving diphenylmethane and potassium phenylacetate, and when condensed with magnesium benzyl chloride yields $\beta\beta$ -diphenyl- $\alpha\alpha$ -dibenzylethyl alcohol, $CHPh_2 \cdot C(C_6H_5)_2 \cdot OH$, m. p. 92—93°, which is also obtained by condensing ethyl diphenylacetate with magnesium benzyl chloride.

W. G.

Molecular Transpositions of α -Glycols. III. The Dehydration of $\alpha\gamma$ -Diphenyl- β -benzylpropan- $\alpha\beta$ -diol. A. ORÉKHOFF (*Bull. Soc. chim.*, 1919, [iv], 25, 111—115. Compare preceding abstract).—[With J. ZIVE.]—Magnesium benzyl chloride condenses with methyl phenylglycolate to give $\alpha\gamma$ -diphenyl- β -benzylpropan- $\alpha\beta$ -diol, $CHPh(OH) \cdot C(CH_2Ph)_2 \cdot OH$, m. p. 110—111°, giving a monoacetyl derivative, m. p. 125—126°. The glycol, when dehydrated with sulphuric acid, yields benzyl $\alpha\beta$ -diphenylethyl ketone, $CH_2Ph \cdot CHPh \cdot CO \cdot CH_2Ph$, m. p. 75—76°, giving an oxime, m. p. 77—78°, and a phenylhydrazone, m. p. 126—127°. This ketone condenses with magnesium benzyl chloride to give $\alpha\beta\delta$ -triphenyl- γ -benzylbutan- γ -ol, $CH_2Ph \cdot CHPh \cdot C(CH_2Ph)_2 \cdot OH$, m. p. 122—123°, identical with the product obtained by the action of magnesium benzyl bromide on methyl $\alpha\beta$ -diphenylpropionate.

W. G.

Molecular Transpositions of the α -Glycols. IV. Product of Dehydration of a Methoxy-derivative of $\alpha\beta$ -Triphenylethanedio. Phenyl Migration. A. ORÉKHOFF (*Bull. Soc. chim.*, 1919, [iv], **25**, 115—118. Compare preceding abstract).—[With F. COMA-Y-ROCA].—Magnesium phenyl bromide condenses with *p*-anisoin to give α -phenyl- $\alpha\beta$ -di-*p*-anisylethane- $\alpha\beta$ -diol,



m. p. 163—164°, which when dehydrated with sulphuric acid yields phenyl-di-*p*-anisylacetaldehyde, $\text{CHO}\cdot\text{CPh}(\text{C}_6\text{H}_4\cdot\text{OMe})_2$, m. p. 88—89°, giving an *oxime*, m. p. 132—133°, and a *semicarbazone*, m. p. 186—187°. This aldehyde is decomposed by alcoholic potassium hydroxide, giving phenyl-di-*p*-anisylmethane, m. p. 100—101° (compare Feuerstein and Lipp, A., 1902, i, 768).

W. G.

β -Bromoethyl *p*-Nitrobenzoate. THE ABBOTT LABORATORIES, (Brit. Pat., 121578).—The β -bromoethyl ester of *p*-nitrobenzoic acid is prepared by heating a salt of *p*-nitrobenzoic acid with an excess of ethylene bromide, preferably in the presence of an amine or of finely divided copper as a catalyst. A mixture of 15 grams of the dry sodium salt, 75 grams of ethylene bromide, and 0.5—1.0 c.c. of diethylamine is heated in a sealed tube at 140° for five hours. The product is neutralised, the excess of ethylene bromide is removed by distillation with steam, and the residue of β -bromoethyl *p*-nitrobenzoate is separated from a small quantity (about 4 grams) of the di-*p*-nitrobenzoic ester of ethylene glycol, which is formed as a by-product, by means of a suitable solvent, such as ether. The yield of crude product is about 15 grams; the pure β -bromoethyl ester has m. p. 51—52°, and may be converted into novocaine (diethylaminoethyl *p*-aminobenzoate) by combination with diethylamine and reduction of the nitro-group.

J. F. B.

Application of Acetylated Phenolcarboxylic Acids to the Synthesis of Depsides. EMIL FISCHER and A. REFIK KADISADÉ (*Ber.*, 1919, **52**, [B], 72—77).—Acetylated phenolcarboxylic acids can be used instead of the methylcarbonato-derivatives for the synthesis of the simpler depsides, but the advantages of the new method over the old are not so marked as in the case of the synthesis of digallic acid (A., 1918, i, 172). 4-*p*-Acetoxybenzoyloxybenzoic acid, $\text{OAc}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, microscopic needles or long leaflets, m. p. 221—223° (corr.) with previous sintering, is precipitated in the form of its sodium salt when an ethereal solution of *p*-acetoxybenzoyl chloride and aqueous sodium hydroxide are added gradually, with cooling, to a solution of *p*-hydroxybenzoic acid in aqueous sodium hydroxide (1 mol.). In a similar way, 4-*p*-hydroxybenzoyloxybenzoic acid is converted into the acetylated tridepside, and *p*-hydroxybenzoic acid and triacetyl-galloyl (triacetoxybenzoyl) chloride yield *p*-triacetoxybenzoyloxy-

benzoic acid, $\text{C}_6\text{H}_5(\text{OAc})_3 \cdot \text{CO} \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, microscopic leaflets, m. p. $172 \rightarrow 173^\circ$ (corr.). C. S.

The Products of the Addition of Benzoic Acid to Aryl Thiocarbimides. H. BECKER and A. BISTRZYCKI (*Helv. Chim. Acta*, 1919, 2, 111—117).—In an earlier paper (A., 1915, i, 245), it was shown that benzoic acid and phenylthiocarbimide react to form *N*-phenyl-*S*-benzhydrylthiocarbamate- α -carboxylic acid. The three *N*-tolyl derivatives, $\text{C}_6\text{H}_4\text{Me} \cdot \text{NH} \cdot \text{CO} \cdot \text{S} \cdot \text{CPh}_2 \cdot \text{CO}_2\text{H}$, have now been obtained from the tolylthiocarbimides in the same way, the yields being excellent; the *ortho*-derivative forms colourless tablets, decomp. 139° , the *meta*-compound decomposes at 141° , and the *para*- at 138.5° .

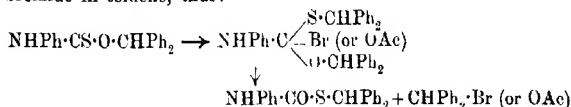
These acids readily lose carbon dioxide when heated at 60 — 100° with pyridine, the products being the *S*-benzhydryl *N*-arylthiocarbamates, $\text{NHAr} \cdot \text{CO} \cdot \text{S} \cdot \text{CHPh}_2$. The *phenyl* derivative forms bundles of needles, m. p. 135 — 136° ; the *o*-tolyl compound crystallises in long needles, m. p. 123.5 — 124.5° ; the *m*-tolyl compound forms glistening leaflets, m. p. 101 — 102.5° ; and the *p*-tolyl derivative forms long prisms, m. p. 149.5 — 151° .

When the acids are boiled with methyl alcohol and concentrated sulphuric acid, they yield internal anhydrides, namely, the 5:5-diphenyl-3-arylthiazolid-2:4-diones, $\text{S} \begin{matrix} \text{CO} \cdot \text{NAr} \\ \text{CPh}_2 \cdot \text{CO} \end{matrix}$, as follows: the 3-phenyl derivative, long, glistening prisms, m. p. 147.5 — 148.5° ; the *o*-tolyl compound, large, granular masses of hexagonal prisms, m. p. 108 — 109° ; the *m*-tolyl compound, rectangular prisms, m. p. 96.5 — 97.5° ; the *p*-tolyl compound, flat needles, m. p. 105.5 — 106.5° .

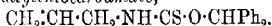
Benzoic and thiobenzoic acids react with undiluted phenylthiocarbimide at 100° to form *s*-diphenylcarbamide. It is reported that this substance suffers decomposition to a certain extent when melted (at about 234°) or distilled (about 260°). J. C. W.

Transformations of some O-Esters of Arylated or Alkylated Thiocarbamic Acids. A. BETTSCHART and A. BISTRZYCKI (*Helv. Chim. Acta*, 1919, 2, 118—132).—In their first communication on the condensation of benzoic acid with arylthiocarbimides in the presence of pure acetic and sulphuric acids (A., 1915, i, 245), Becker and Bistrzycki offered an explanation of the mechanism of the unusual reaction, which has now been tested and found to be justified. They assumed that the first product was the expected *O*-ester, $\text{NHAr} \cdot \text{CS} \cdot \text{O} \cdot \text{CPh}_2 \cdot \text{CO}_2\text{H}$. Attempts to isolate such esters have failed, but closely related substances, with which the theory can be tested, have now been obtained by the action of the thiocarbimides on the sodium compound of benzhydrol dissolved in xylene. These esters may be transformed readily into the *S*-esters, $\text{NHAr} \cdot \text{CO} \cdot \text{S} \cdot \text{CHPh}_2$, by boiling with glacial acetic acid, although in the case of the phenyl compound many other methods have been found, including heating at

130—135°, or treatment with cold hydrochloric acid. The transformations by means of acids are explained by assuming that a little benzhydrol is liberated by hydrolysis, and is then attached at the -C:S group in the form of its acetate or chloride, which is then eliminated again from the other position. Theoretically, therefore, a trace of such an ester should cause the transformation of an unlimited amount of *O*-ester into *S*-ester, and the whole theory is neatly proved by the fact that the change can indeed be brought about by heating with a small quantity of benzhydrol acetate or bromide in toluene, thus:



The following *O*-benzhydrol *N*-arylthiocarbamates are described; their isomerides have been made in the above manner, but are also mentioned in the previous abstract: The *phenyl* derivative, quadratic prisms, m. p. 123—123.5°; the *o*-tolyl compound, m. p. 123.5—124° (decomp.); and the *p*-tolyl compound, decomp. 126.5°. *O*-Benzhydrol *N*-allylthiocarbamate,

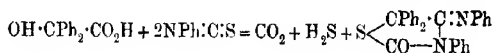


has also been prepared, in quadratic prisms, m. p. 59.5—61.5°, and converted into the *isomeride*, $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{S}\cdot\text{CHPh}_2$, which forms very long prisms, m. p. 114.5—116.5°.

This transformation seems to depend on the nature of the group which wanders, for the benzyl derivative, $\text{NHPh}\cdot\text{CS}\cdot\text{O}\cdot\text{CH}_2\text{Ph}$, is not so changed by acetic acid.

Benzilic acid will not condense with alkylthiocarbimides under the conditions employed in the earlier cases, but if phosphoric oxide is added as well as sulphuric acid, the same kind of reaction takes place. Ordinary mustard oil gives *N*-allyl-*S*-benzhydrolthiocarbamate- α -carboxylic acid, $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{S}\cdot\text{CPh}_2\cdot\text{CO}_2\text{H}$, prisms, decomp. about 133°, which is quantitatively converted into α -thioldiphenylacetic acid by boiling with 1% potassium hydroxide (a more convenient preparation than the earlier one, *loc. cit.*), or may be changed into the above *S*-benzhydrol *N*-allylthiocarbamate by heating with pyridine. *N*-iso-Butyl-*S*-benzhydrolthiocarbamate- α -carboxylic acid, rhombic tablets, m. p. 123—124° (decomp.), and *S*-benzhydrol *N*-isobutylthiocarbamate, long, silky prisms, m. p. 73.5—75°, have also been obtained.

In the hope of getting a normal *O*-ester from benzilic acid and phenylthiocarbimide, these substances have been heated together without diluents at 100°. A reaction, represented by the equation



was found to take place, the product being 4-phenylimino-3:5:5-triphenylthiazolid-2-one, which crystallises in prisms, m. p.

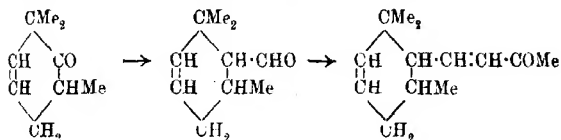
162.5—163.5°, and yields the 3:5:5-triphenylthiazolid-2:4-dione, mentioned in the previous abstract, when boiled with acetic and sulphuric acids.

J. C. W.

Preparation of Benzaldehyde. THE DOW CHEMICAL COMPANY (U.S. Pat., 1272522).—Benzyl bromide is mixed with a solution of sodium nitrate or calcium nitrate, and the mixture is heated at about the boiling point with constant agitation; the benzaldehyde produced is then separated from the aqueous solution of sodium bromide and nitrous acid. The reaction takes place between equimolecular proportions of benzyl bromide and sodium nitrate, and the benzaldehyde is practically a pure product, whereas that produced with benzyl chloride and lead nitrate is always contaminated with benzoic acid.

J. F. B.

Preparation of Polymethylcyclohexenones of the Iron Type. L. RUZICKA (*Helv. Chim. Acta*, 1919, 2, 144—161).—For the synthesis of perfumes of the type of iron, the author argues that it is important to start from compounds in which the ethylene linking in the cyclohexene ring is already fixed, such methods as those described by Merling and Velde, for example (A., 1909, i, 479), being open to question on this point. The conversion of a cyclohexenone of the desired type into iron or a similar compound would be quite a simple matter; thus:



The present communication describes the preparation of two such cyclohexenones, but the yields are so poor that further developments along these lines seem to be useless.

The desired cyclohexenones should be most readily obtained from the corresponding unsaturated dicarboxylic acids, and these from δ ketonic esters by Reformatzky's method. The chief obstacle is the closing of the ring in the case of the dicarboxylic esters. Two examples are given.

A. Preparation of the δ Ketonic Esters.— δ -Ketohectic acid may be prepared most readily by the interaction of ethyl sodioacetate and ethyl β -iodopropionate. With suitable apparatus, it may also be obtained by heating dihydroresorcinol with barium hydroxide and water at 150°. A third method, giving poor results, is as follows: fresh ethyl methylenemalonate is treated with ethyl sodioacetate solution at 0°, and the ethyl δ -ketopentane- α -tricarboxylate so formed, b. p. 198—200°/15 mm., is boiled with dilute hydrochloric acid. The δ -ketohectic acid is readily esterified by boiling with alcohol containing a little hydrogen chloride.

Ethyl δ -keto- α -methylhectoate, b. p. 110—112°/13 mm., and the

free acid, b. p. 157—159°/13 mm., are prepared by the interaction of a solution of ethyl sodioacetoacetate and ethyl methylacrylate, followed by boiling the ethyl ϵ -ketoheptane- $\beta\delta$ -dicarboxylate so formed, b. p. 152—156°/12 mm., with hydrochloric acid.

Ethyl δ -keto- $\alpha\alpha$ -dimethylhexoate, b. p. 110—115°/13 mm., is obtained from the acid, this being formed by heating methyl 4:6-diketo-2:2-dimethylcyclohexane-1-carboxylate (from mesityl oxide and methyl sodiomalonate) with barium hydroxide and water at 150° (compare Bredt, A., 1898, i, 264).

B. Condensations of the δ -Ketonic Esters with Ethyl α -Bromo-isobutyrate.—These condensations are brought about by means of zinc turnings, and the lactonic esters are isolated in the usual way. Ethyl δ -ketoheptate gives the lactone of δ -hydroxy- ϵ -carbethoxy-

$\delta\epsilon$ -dimethylheptonic acid, $\text{CO}_2\text{Et}\cdot\text{CMe}_2\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}-\text{CO}-\text{CH}_2$, m. p.

176—177°. Ethyl δ -keto- α -methylhexoate yields the lactone of δ -hydroxy- ϵ -carbethoxy- $\alpha\delta\epsilon$ -trimethylheptonic acid, b. p. 169—171°/12 mm., and the third ester produces the lactone of δ -hydroxy- ϵ -carbethoxy- $\alpha\alpha\delta\epsilon$ -tetramethylheptonic acid, b. p. 170—175°/12 mm.

C. Hydrolysis of the δ -Lactonic Esters.—The first two lactones are readily hydrolysed to the esters of unsaturated dicarboxylic acids by boiling them with alcoholic hydrogen bromide, but the third lactone has a very stable ring. $\beta\gamma$ -Dimethyl- Δ^1 -heptene- $\beta\delta$ -dicarboxylic acid, $\text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{CMe}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, from the first lactone, forms stout needles, m. p. 108—109°, gives an ethyl ester, b. p. 153—157°/12 mm., and yields acetic, isobutyric, and succinic acids on oxidation with permanganate. $\beta\gamma$ -Dimethyl- Δ^1 -heptene- $\beta\delta$ -dicarboxylic acid, from the second lactone, has m. p. 84—85°, and its ethyl ester has b. p. 153—157°/12 mm.

D. Preparation of the Polymethylcyclohexenones.—When the ester of the above hexenedicarboxylic acid is boiled with sodium powder in benzene, it yields a small quantity of ethyl 4-keto-2:3:3-trimethyl- Δ^1 -cyclohexene-1-carboxylate, most of the material suffering complex condensation. This ester gives 2:3:3-trimethyl- Δ^1 -cyclohexen-4-one on hydrolysis, b. p. 85—90°/12 mm.; semicarbazone, m. p. 168—171°. When methylated and then hydrolysed, it also forms 2:3:3:5-tetramethyl- Δ^1 -cyclohexen-4-one, b. p. 90°/12 mm.; semicarbazone, m. p. 196—197°.

Displacement of the ethylene linking occurs if the unsaturated dicarboxylic acids are heated with acetic anhydride and then distilled. The hexenedicarboxylic acid yields 3:4:4-trimethyl- Δ^1 -cyclohexen-5-one, b. p. 85—90°/14 mm., semicarbazone, m. p. 185—187°, which may be reduced by sodium and alcohol to 1:2:2-trimethylcyclohexan-3-ol, b. p. 85—87°/15 mm. The heptenedicarboxylic acid yields 3:4:4:6-tetramethyl- Δ^1 -cyclohexen-5-one, b. p. 80—85°/13 mm.; semicarbazone, m. p. 178—179°.

J. C. W.

The Reduction of Aromatic Ketones. W. D. COHEN (Rec. trav. Chim., 1919, 38, 113—131).—In continuation of previous

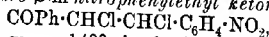
work (compare this vol., i, 124), the author has studied the reduction of a number of substituted benzophenones by aluminium amalgam in alcohol, and determined the proportions of substituted benzhydrol and benzopinacone formed in each case. The proportion of benzhydrol to benzopinacone is found to depend directly on the velocity with which the pinacone is decomposed in alkaline solution to give the hydrol and the ketone. Thus, then aluminium amalgam is, at the moment of reduction, a slightly alkaline reagent and promotes the secondary reaction, the products of which are dependent on the velocity with which the primary product, the pinacone, is attacked. The course of the reaction in the reduction of benzophenone consists of the preliminary formation of diphenylhydroxymethyl, CPh_2OH , which is immediately transformed into pinacone.

o-Chlorophenyl *p*-tolyl ketone, m. p. 99.5° , is obtained by the condensation of *o*-chlorobenzoyl chloride with toluene in the presence of aluminium chloride. It yields 2-chloro-4'-methylbenzhydrol, m. p. 67° , and 2-chloro-4'-methylbenzopinacone, m. p. $175\text{--}176^\circ$. *p*-Chlorophenyl *p*-tolyl ketone, m. p. 118° , similarly prepared, gives only the corresponding hydrol, m. p. 67.5° , by reduction in neutral solution, and the pinacone, m. p. 178° , by reduction in acid solution.

W. G.

Some Ketone Condensation Reactions. SVEN BODFORSS (*Ber.*, 1919, 52, [B], 142—145).—The author has shown (A., 1917, i, 223; 1918, i, 229) that Widman's reaction (A., 1913, i, 1219; 1916, i, 406; 1917, i, 221) is not a general one for aldehydes. It is of interest, therefore, to ascertain what course the Erlenmeyer reaction will take when derivatives of chloroacetic acid other than the ethyl ester are employed. An alcoholic solution of benzaldehyde ($1\frac{1}{2}$ mols.) and chloroacetanilide cooled in a freezing mixture yields by treatment with sodium ethoxide solution and subsequent acidification with dilute acetic acid $\alpha\beta$ -*orido*- β -phenylpropionanilide, $\text{CHPh} \begin{array}{c} \diagup \\ \text{O} \end{array} \text{CH} \cdot \text{CO} \cdot \text{NHPh}$, colourless needles, m. p. 142° .

Phenyl $\alpha\beta$ -dichloro- β -*m*-nitrophenylethyl ketone,



colourless crystals, m. p. 148° , is obtained by saturating a glacial acetic acid solution of ω -chloroacetophenone and *m*-nitrobenzaldehyde with hydrogen chloride in the cold, and also by leading chlorine into a solution of phenyl *m*-nitrostyryl ketone in the same solvent.

Cuminaldehyde and acetophenone, condensed by means of methyl-alcoholic sodium methoxide, yield phenyl isopropylstyryl ketone, $\text{C}_6\text{H}_4\text{Pr}^s \cdot \text{CH} : \text{CH} \cdot \text{COPh}$, b. p. $225\text{--}227^\circ/15$ mm. (slight decomp.), which forms a dibromide, needles, m. p. $119\text{--}119.5^\circ$.

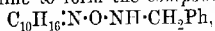
C. S.

Theory of Colour Lakes. Action of Potassium Ferricyanide on Alizarin in Alkaline Solution and the Constitution of Hydroxyanthraquinones. OSKAR BAUDISCH (*Ber.*, 1919, 52, [B], 146—147).—A claim of priority over Scholl and Zinke

(this vol., i, 25. Compare also Baudisch, A., 1917, i, 356, 556; Baudisch and Klaus, *ibid.*, i, 331). C. S.

Optically Active Pinene Nitrosochloride, and Synthetic Active Pinene. E. V. LYNN (*J. Amer. Chem. Soc.*, 1919, **41**, 361—368).—In the preparation of the nitrosochloride from pinene by Wallach's method, it is well known that the yield of crystalline product varies inversely with the optical activity of the specimen, whilst the mother liquor remains blue for some time with the most active oils. An obvious suggestion, therefore, is that the active nitrosochlorides are more soluble than the inactive one, but Tilden offered another explanation of the poor yield (T., 1904, **85**, 759—764). By varying the conditions of the experiment, somewhat better yields may be obtained and the active nitrosochlorides actually isolated.

Equal volumes of pinene, ethyl nitrite, and alcohol are mixed and treated at -5° with the requisite amount of hydrogen chloride dissolved in alcohol. Crystals of inactive pinene nitrosochloride are removed after half an hour, and the mother liquor is then diluted with alcohol and left at -10° , when the active modification gradually separates. The dextro-variety was obtained in this instance from American turpentine, and the lævo-modification from Oregon or Canada balsams. Active pinene nitrosochloride crystallises in transparent or cotton-like needles, m. p. $81-81.5^{\circ}$, $[\alpha]_D \pm 322^{\circ}$, and is appreciably soluble in most organic media. It reacts with benzylamine to form the compound,



m. p. $144-145^{\circ}$, $[\alpha]_D \pm 92^{\circ}$ in acetone, and with piperidine to give a similar compound, crystallising in rosettes, m. p. 84° , $[\alpha]_D \pm 50^{\circ}$. With alcoholic alkali hydroxide, it reacts to form nitrospinene, and with aniline to give aminoazobenzene and active pinene; b. p. $155-159^{\circ}$, $n_D 1.470$, $[\alpha]_D \pm 53.75^{\circ}$ in 4% alcoholic solution. This "regenerated" *d*-pinene gave an inactive hydrochloride, like the natural product.

The existence of active nitrosochlorides in the mother liquors does not by any means fully account for the poor yields. Even inactive pinene only gives about 50% of the theoretical yield. As the blue solution deposits its colourless crystals, a gas is evolved which Tilden suggested might be nitrous oxide. It is now conclusively proved to be nearly pure nitrogen, and its volume agrees closely with that of the nitrogen unaccounted for. The mother liquor has been briefly examined, and found to be a complex mixture. J. C. W.

Keto-cineole. GUIDO CUSMANO (*Gazzetta*, 1919, **49**, i, 26—38).—When heated with ethyl alcohol, α -terpineol nitrosochloride is converted in satisfactory yield into keto-cineole-oxime, and this with nitrous acid gives quantitatively the pernitroso-compound, from which the free ketone is obtained, also quantitatively, by treatment with concentrated aqueous ammonia (compare Cusmano and Linari, A., 1912, i, 272).

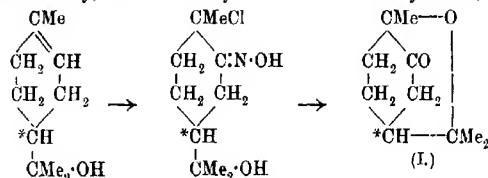
Saturated cyclic ketones containing ten carbon atoms in the molecule and possessing the $\cdot\text{CO}\cdot\text{CH}_2\cdot$ grouping and the general structure of keto-cineole may be divided into two groups: (1) menthone, tetrahydrocarvone, and tanacetone, and (2) camphor and pinocamphone. All show the same reactions of the carbonyl and of the adjacent methylene group, and opening of the fundamental hexamethylene nucleus between the carbonyl and the neighbouring tertiary (or quaternary) carbon atom is possible in all cases; rupture between the carbonyl and the methylene in addition is, however, possible only with the ketones of the second group. With the latter, which possess a "bridge," keto-cineole must be classed. Keto-cineole exhibits marked physiological activity, which is to be investigated.

Reduction of keto-cineole oxime by means of sodium and boiling amyl alcohol yields as one product an *aminocineole*, which forms a crystalline *platinichloride*, $(\text{C}_{10}\text{H}_{17}\cdot\text{O}\cdot\text{NH}_2)_2\cdot\text{H}_2\text{PtCl}_6\cdot 2\text{H}_2\text{O}$, m. p. 233° (decomp.).

Inactive keto-cineole forms shining, white, lamellar crystals, m. p. 42° , and yields a *semicarbazone*, m. p. 220° , and a *phenylhydrazone*, $\text{C}_{10}\text{H}_{16}\cdot\text{O}\cdot\text{N}_2\cdot\text{HPh}$, m. p. about 160° , which gradually loses phenylhydrazine.

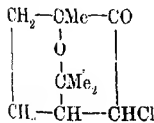
The use of inactive α -terpineol mixed with some of the dextro-rotatory form results in the formation of inactive and active keto-cineole-oximes. The active oxime forms prismatic crystals, m. p. 168° , $[\alpha]_D^{25}$ in methyl alcohol -11.8° . The active keto-cineole forms colourless, lamellar crystals, m. p. about 50° , $[\alpha]_D^{25} -44.0^\circ$.

Although keto-cineole contains two asymmetric carbon atoms, the optical activity, as is shown by the scheme of the synthesis,



is due only to the one marked with an asterisk, this being pre-existent in the active α -terpineol. T. H. P.

Halogenated Compounds of Keto-cineole. GUIDO CUSMANO (*Atti R. Accad. Lincei*, 1919, [v], **28**, i, 78—83. Compare preceding abstract).—Keto-cineole is readily converted into monochloro-(or monobromo-)keto-cineole (annexed formula), but further halogenation results in the formation of derivatives of carvomenthone (tetrahydrocarvone). The structure of the monohalogenated compounds is established by the action of potassium permanganate (three atoms of oxygen per molecule of halogen derivative) or of dilute potassium hydroxide solution, which



converts them into cineolic acid, this reaction being similar to the transformation of analogous camphor derivatives into camphoric acid. When treated with hydrogen bromide in ethereal solution, keto-cineole yields 1:8-dibromocarvomenthone (*loc. cit.*); the latter, and not 1:3:8-tribromocarvomenthone, is also obtained by the action of hydrogen bromide on monobromoketo-cineole under similar conditions, transformation of the cineole "bridge" being accompanied by elimination by reduction of the bromine atom from the methylene group next to the carbonyl.

Monochloroketo-cineole, $C_{10}H_{15}O_2Cl$, forms shining, elongated prisms, m. p. 78° , and volatilises unchanged (compare Cusmano, this vol., ii, 61).

Monobromoketo-cineole, $C_{10}H_{15}O_2Br$, forms transparent, colourless, prismatic crystals, m. p. about 90° , and when volatilised emits an odour of keto-cineole. By bromine (2 atoms per mol.) in chloroform solution, it is converted into a compound, which crystallises in nacreous, lamellar crystals, m. p. 143° , and appears to be a tetrabromotetrahydrocarvone, $C_{10}H_{14}OBr_4$. T. H. P.

Digitalis Glucosides. XXXIX. H. KILIANI (*Ber.*, 1919, 52, [B], 200—205).—After many years of disappointment, the author has now succeeded in degrading a compound of the digitalis series, namely, digitogenic acid (A., 1902, i, 46), to simpler substances which may open up the way to a final elucidation of the composition of the glucosides.

When heated at 100° with ten times its volume of 50% alcohol and concentrated hydrochloric acid in the proportion 25:1, digitogenic acid is hydrolysed to a lactone, $C_8H_{12}O_2$ (this may be corrected in the future), m. p. 93° , $[\alpha]_D -79.5^\circ$, and a monobasic acid, $C_{20}H_{32}O_8$ (or $C_{20}H_{30}O_8$), which crystallises well from diluted acetic acid with $0.5H_2O$, has m. p. 112° , $[\alpha]_D -79.8^\circ$, and forms a magnesium salt with $6H_2O$. J. C. W.

Saponins. I. E. WINTERSTEIN and M. MAXIM (*Helv. Chim. Acta*, 1919, 2, 195—203).—A short summary of the present knowledge of saponins is given, and attention is directed to the need for more extensive studies of the saponins which remain when these glucosides are hydrolysed. For a preliminary investigation of this sort, the authors have chosen the saponins of the horse-chestnut and the soap-berry (*Sapindus saponaria*). These may be isolated as follows. The crushed or powdered material is extracted with ether, then with warm 95% alcohol in the presence of calcium carbonate, and the alcoholic extract is evaporated, diluted with water, and digested with lead hydroxide for several days. After filtering and removing lead from the filtrate, the solution is concentrated in a high vacuum. For the further purification of the saponins, dialysis may be advisable, as the plant material contains a good deal of sucrose.

Horse-chestnut saponin is readily hydrolysed by dilute acids in the cold. *Sapindus saponin*, however, is only partly degraded by

cold acids. It appears to be a mixture of glucosides, which gives a mixture of pentosides when partly hydrolysed ("initial sapogenins"), these being converted into the "end sapogenins" by means of warm acids. A pentoside is also formed when the saponin is left with dilute hydrogen peroxide at 40° for some days. The sugars present include *d*-fructose and *d*-glucose, and rhamnose and arabinose in the ratio 1:2 or 1:3, and the approximate composition of the saponin is roughly 33—35% "end sapogenin," 45% hexoses, and 15% pentoses.

Sapindus saponin may be brominated in methyl-alcoholic solution. The product has just the same foaming power as the original saponin, but is no longer hæmolytic; in fact, it hinders the hæmolytic activities of other saponins.

Only about 6 grams of pure sapogenin can be obtained from 100 grams of the crude saponin. The compound, $C_{18}H_{32}O_8$, has m. p. 319°, forms a mono-acetate, gives a fluorescent dye when condensed with resorcinol, and yields naphthalene derivatives on oxidation.

J. C. W.

Curcumin. PRAPHULLA CHANDRA GHOSH (T., 1919, 115, 292—299).

Tannins. I. Hamameli-tannin. KARL FREUDENBERG (*Ber.*, 1919, 52, [B], 177—185).—Although the constitutions of Chinese and Turkish tannins have been elucidated in all essential points by the work of Fischer and his collaborators (1912—1918), the last remaining problems will evidently require time for their solution, because these naturally occurring amorphous substances are very probably inseparable mixtures of very nearly related polygalloyl-glucoses. Grüttner's hamameli-tannin is, however, a crystalline, and therefore probably individual, substance. With regard to its constitution, the only fact known is that it contains gallic acid and a new sugar (Fischer, A., 1913, i, 1352). Titration shows that there is no free carboxyl group. By treatment with diazomethane in acetone solution, hamameli-tannin yields a friable methyl derivative which yields gallic acid trimethyl ether by hydrolysis with *N*-sodium hydroxide. The prolonged treatment with 5% sulphuric acid required to hydrolyse the tannin also causes changes in the sugar produced. The author has therefore hydrolysed a dilute aqueous solution of the tannin covered with toluene with tannase (the preparation of which is described; dextrose must be removed), and obtained gallic acid and a sugar (calculated as a hexose) in quantities corresponding with the formula of a digalloyl-hexose.

The sugar, which has been obtained only as a yellow, viscous, levorotatory syrup, has not been identified; it appears to contain a normal chain of six carbon atoms.

C. S.

Formation of Flavone or Coumarone Derivatives from Hydroxychalkones. J. TAMBOR and HANS GUBLER (*Helv. Chim. Acta*, 1919, 2, 101—111).—Tambor has recently developed an easy

method for the synthesis of hydroxyflavones, namely, by the action of alcoholic potassium hydroxide on the dibromides of acetoxychalkones (A., 1916, i, 831), and Oesterle and Kueny have used this process in showing the connexion between homoeriodictyol and luteolin (A., 1917, i, 703). It is now shown, however, that flavones are not always formed, coumarones or coumaranones resulting in some cases. Whether the five- or six-membered oxygen ring is formed seems to depend on the position of the substituents in the aldehyde component of the chalkone.

2':4':2-Trihydroxychalkone (2:4-dihydroxyphenyl 2-hydroxystyryl ketone) (Göschke and Tambor, A., 1912, i, 196) is converted into the *triacetate*, glistening needles, m. p. 170–171°, and the *dibromide* of this, which crystallises in long needles, m. p. 144°, is warmed with alcoholic potassium hydroxide, and thus condensed to 2':4'-dihydroxy-1-benzoylcoumarone, $\text{C}_6\text{H}_4 \begin{array}{c} \text{O} \cdot \text{C} \cdot \text{CO} \cdot \text{C}_6\text{H}_3(\text{OH})_2 \\ \diagup \quad \diagdown \\ \text{CH} \end{array}$.

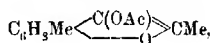
This crystallises as a woolly mass of yellow needles, m. p. 144°, forms a colourless *diacetate*, m. p. 119°, and may be synthesised by the condensation of resorcinol with coumarilic chloride in the presence of aluminium chloride.

The methyl ethers of this coumarone are not easily obtained by direct methylation. They have been prepared by Rap's method for synthesising 1-benzoylcoumarones (A., 1896, i, 303), namely, by the interaction of salicylaldehyde and the mono- or di-methyl ethers of *o*-chlororesacetophenone (A., 1918, i, 395). 2'-Hydroxy-4'-methoxy-1-benzoylcoumarone forms small, lemon-yellow tablets, m. p. 253° (decomp.), and its *acetate* has m. p. 166°; 2':4'-dimethoxy-1-benzoylcoumarone forms colourless prisms, m. p. 102°. Other benzoylcoumarones prepared incidentally, in the same way, include 2'-hydroxy-4':6-dimethoxy-1-benzoylcoumarone, dark yellow tablets, m. p. 253° (decomp.) (*acetate*, m. p. 180°), from 2-hydroxy-3-methoxybenzaldehyde and *o*-chlororesacetophenone monomethyl ether, and 4'-hydroxy-6-methoxy-1-benzoylcoumarone, small, dull yellow prisms, m. p. 189°, from the same aldehyde and *o*-chloro-*p*-hydroxyacetophenone.

The influence of the position of the substituents is further illustrated by another example. 2-Acetoxyphenyl 4-methoxystyryl ketone dibromide yields *p*-methoxybenzylidenecoumaranone when treated with concentrated potassium hydroxide (Herstein and Kostanecki, A., 1899, i, 369), whereas 2-acetoxyphenyl 2-methoxystyryl ketone dibromide gives 2'-methoxyflavone. *o*-Hydroxyacetophenone and *o*-methoxybenzaldehyde are condensed by means of sodium hydroxide to 2-hydroxyphenyl 2-methoxystyryl ketone, yellow needles, m. p. 112°, the *acetate* of which, m. p. 64°, is converted into the *dibromide*, $\text{OAc} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CHBr} \cdot \text{CHBr} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$, m. p. 101° (decomp.), and then into 2'-methoxyflavone (2'-methoxy-3-phenyl- γ -benzopyrone), m. p. 103°, as indicated (compare A., 1912, i, 486). For comparison with *o*-methoxybenzylidenecoumaranone, this has been synthesised from coumaranone and *o*-methoxybenzaldehyde; it crystallises in straw-yellow prisms, m. p. 175°.

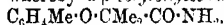
Other *benzylidenecoumaranones*, prepared from suitable aldehydes and coumaranone, are as follows: 2-hydroxy-3-methoxy-, yellow needles, m. p. 212° (decomp.) (acetate, very pale yellow, silky needles, m. p. 176°); 2:3-dimethoxy-, long, pale yellow needles, m. p. 130°; 2:4-dimethoxy-, slender, bright yellow needles, m. p. 182—183°; 4-dimethylamino-, $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{O} \\ \diagdown \text{CO} \end{array} \text{C}:\text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$, very dark red needles, m. p. 170—172°. J. C. W.

Alkylated Coumaranones, especially 1:1:4-Trimethylcoumaranone. K. VON AUWERS and H. SCHÜTTE (*Ber.*, 1919, 52, [B], 77—92).—The production of *O*- and of *C*-alkyl derivatives of certain types of coumaranones has been already described (Auwers, A., 1912, i, 484, 486). The parent coumaranones have now been examined. 1:4-Dimethylcoumaranone, b. p. 138—140°/22 mm., which is best purified by distillation (A., 1915, i, 440), yields by acetylation 2-acetoxy-1:4-dimethylcoumaranone,



stout crystals, m. p. 29—30°, b. p. 170.5—171.5°/28 mm., which is converted into 1-chloro- and 1-bromo-1:4-dimethylcoumaranone, respectively, by chlorine or bromine in carbon disulphide solution, and easily undergoes fission by treatment with warm acids, being converted, therefore, by *p*-nitrophenylhydrazine hydrochloride in aqueous-alcoholic solution into 4-hydroxy-*m*-tolyl methyl diketone di-*p*-nitrophenylhydrazone (A., 1918, i, 193).

1:4-Dimethylcoumaranone forms an *acime*, $\text{C}_{10}\text{H}_{11}\text{O}_3\text{N}$, colourless needles, m. p. 129°. The ketone, which yields chiefly the *O*-methyl derivative by shaking with methyl sulphate and sodium hydroxide solution (A., 1918, i, 27), is converted mainly into 1:1:4-trimethylcoumaranone by boiling with methyl iodide and sodium methoxide solution, or, better, by treatment with sodamide and methyl iodide in ethereal solution; in the former method about 30%, and in the latter about 5%, of the *O*-ether is produced. The *O*-ether is separated by conversion into the semicarbazone. The proof that the new methyl group is attached in position 1 is obtained indirectly by showing that 1:4-dimethylcoumaranone by ethylation and 4-methyl-1-ethylcoumaranone by methylation, as above, yield the same 1:4-dimethyl-1-ethylcoumaranone, b. p. 135—135.5°/18 mm., D_4^{20} 1.056, n_D^{20} 1.5359 (semicarbazone, colourless needles, m. p. 184—187°). A second proof is furnished by heating 1:1:4-trimethylcoumaranone with sodamide in boiling benzene or toluene, whereby *α*-*tolyl*oxyisobutyramide,



colourless prisms, m. p. 84—85°, is obtained.

C. S.

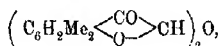
Coumaranones and Hydrindones. KARL VON AUWERS and ELISABETH AUFFENBERG (*Ber.*, 1919, 52, [B], 92—113).—In connexion with the conversion of benzylidene derivatives of substituted

coumaranones into flavonols (Auwers and Pohl, A., 1914, i, 981) and the fission of the furan ring of coumaranones by semicarbazide and certain arylhydrazines (Auwers and Müller, A., 1918, i, 27), the evidence hitherto obtained has allowed certain generalisations to be made regarding the influence of substituents on the stability of the furan ring (Auwers and Müller, *loc. cit.*). To fortify this evidence, the behaviour of a further series of coumaranones towards semicarbazide and towards *p*-nitrophenylhydrazine has been examined. The coumaranone is treated with semicarbazide hydrochloride ($2\frac{1}{2}$ — $3\frac{1}{2}$ mols.) and sodium acetate in aqueous-alcoholic solution at 40 — 50° for three to four days, or is heated on the water-bath for a few hours with *p*-nitrophenylhydrazine hydrochloride in aqueous-alcoholic solution; according as the product is a mono- or di-semicarbazone or a mono- or di-*p*-nitrophenylhydrazone, the furan ring of the coumaranone has not or has been ruptured. Thus 4-methoxycoumaranone yields the semicarbazone, $C_{10}H_{11}O_3N_3$, colourless needles, m. p. 225 — 226° , 5-methoxycoumaranone yields the semicarbazone, $C_{10}H_{11}O_3N_3$, faintly yellow needles, m. p. 213 — 215° , 3:5-dimethylcoumaranone yields the semicarbazone, $C_{11}H_{13}O_3N_3$, colourless needles, m. p. 249 — 251° , and the *p*-nitrophenylhydrazone, $C_{10}H_9O_3N_5$, red needles, m. p. 233° , coumaranone yields *o*-hydroxyphenylglyoxaldi-*p*-nitrophenylhydrazone,

$OH \cdot C_6H_4 \cdot C(N \cdot NH \cdot C_6H_4 \cdot NO_2) \cdot CH \cdot N \cdot NH \cdot C_6H_4 \cdot NO_2$, brownish-red, crystalline powder, m. p. about 265° , 5-methylcoumaranone yields 2-hydroxy-*p*-tolylglyoxaldi-*p*-nitrophenylhydrazone, m. p. about 260° , 6-methylcoumaranone yields 2-hydroxy-*m*-tolylglyoxaldi-*p*-nitrophenylhydrazone, $C_{21}H_{18}O_5N_5$, brownish-violet, crystalline powder, m. p. about 270° , 5-methoxycoumaranone yields 2-hydroxy-4-methoxyphenylglyoxaldi-*p*-nitrophenylhydrazone, $C_{21}H_{18}O_6N_5$, brownish-violet, crystalline powder, m. p. 264° , and 4-methoxycoumaranone yields 2-hydroxy-5-methoxyphenylglyoxaldi-*p*-nitrophenylhydrazone, reddish-brown, crystalline powder, m. p. 264° . 1:1:4-Trimethylcoumaranone (preceding abstract) yields a *p*-nitrophenylhydrazone, $C_{17}H_{17}O_3N_3$, canary-yellow needles, m. p. 148° . The results confirm the generalisations previously made, to which a fourth is now added, namely, the furan ring of 1:1-dialkylcoumaranones is characterised by its special stability.

Since it is possible that the varying stability of the coumaranones towards ketone reagents may be conditioned by their varying tendency to undergo enolisation, the behaviour of the substances during acetylation and during bromine titration by Meyer's method has been examined. No differences could be detected. All the coumaranones acetylate smoothly (of course, provided there is a hydrogen atom in position 1). Meyer's bromine method shows that the coumaranones in question (that is, coumaranones which do not contain an acyl substituent in position 1 [compare Auwers, A., 1912, i. 484, 1009]) are almost entirely ketonic in the solid state, in the fused state, and even after keeping in alcoholic solution for several days. 5-Methoxycoumaranone yields 2-acetoxy-5-

methoxycoumarone, colourless needles, m. p. 74—76°, by treatment with cold pyridine and acetyl chloride, and 3:5-dimethylcoumaranone yields 2-acetoxy-3:5-dimethylcoumarone, colourless needles, m. p. 65—66°, by boiling with acetyl chloride, and 1-bromo-3:5-dimethylcoumaranone, yellow needles, m. p. 105°, softening at 103°, by treatment with bromine in carbon disulphide solution; the bromo-derivative is converted by sodium carbonate in boiling aqueous acetone into the ether,



colourless needles, m. p. 210—212°.

Since α -hydrindones are allied to coumaranones in structure, it is not impossible that they also might be ruptured in the 5-ring by ketone reagents. However, the following hydrindones all react normally with semicarbazide and with *p*-nitrophenylhydrazine: 1-hydrindone yields a semicarbazone, and *p*-nitrophenylhydrazine, $\text{C}_{15}\text{H}_{15}\text{O}_2\text{N}_3$, brownish-red leaflets (from xylene) or orange, crystalline powder (from glacial acetic acid), m. p. 234—235°, 2-methyl-1-hydrindone yields a semicarbazone, colourless, crystalline powder, m. p. 200° with previous softening, and a *p*-nitrophenylhydrazine, brownish-red, microscopic crystals, m. p. 167—168°, 2-phenyl-1-hydrindone forms a semicarbazone, stout crystals, m. p. 211—212°, and a *p*-nitrophenylhydrazine, red crystals and yellow leaflets, both having m. p. 174°, and changeable the one into the other by crystallisation from suitable solvents, 3-phenyl-1-hydrindone forms a semicarbazone, colourless crystals, m. p. 223—225°, darkening at 218°, and a *p*-nitrophenylhydrazine, brick-red crystals, m. p. 220—221°, and 6-methoxy-2-methyl-1-hydrindone, b. p. 148°/10 mm., D_4^{20} 1.116, D_4^{25} 1.1188, n_D^{20} 1.55310, n_D^{25} 1.55884, n_D^{30} 1.57529 at 16.9°, prepared from β -*p*-methoxyphenyl- α -methylpropionyl chloride, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{COCl}$, b. p. 167°/23 mm. (the acid itself, $\text{C}_{13}\text{H}_{14}\text{O}_3$, colourless needles and prisms, m. p. 40°, b. p. 308°, is obtained from ethyl *p*-methoxy- α -methylcinnamate, b. p. 176—177°/15 mm., D_4^{20} 1.0894, D_4^{25} 1.085, n_D^{20} 1.56213, n_D^{25} 1.57009, n_D^{30} 1.59339 at 15.6°, which is itself obtained by warming Wallach's ethyl β -hydroxy- β -*p*-methoxyphenyl- α -methylpropionate with phosphoryl chloride), forms a semicarbazone, colourless, crystalline powder, m. p. 215—216°, and *p*-nitrophenylhydrazine, yellow needles, m. p. 163—164°.

Since the hydrindone last mentioned corresponds in structure with 4-methoxy-1-methylcoumaranone, which is most easily ruptured by semicarbazide, it is improbable that any member of the hydrindone series can be ruptured by ketone reagents. None of them exhibits the character of an enol; they cannot be acetylated and do not absorb bromine in the Meyer titration method. Only in one case has the 5-ring of a hydrindone given evidence of instability; 2-phenyl-1-hydrindone, after exposure to air for three months, yields β -deoxybenzoic-*o*-carboxylic acid by auto-oxidation (compare Salway and Kipping, T., 1909, 95, 116).

C. S.

Spectrochemistry of Coumaranones and of Allied Bicyclic Ketones. K. VON AUWERS (*Ber.*, 1919, **52**, [B], 113—129).—It has been shown (preceding abstracts) that the coumaranones behave as desmotropic substances towards chemical reagents, but in the solid or fused state are almost entirely ketonic. The same conclusion is reached on spectrochemical evidence. For coumaranones of the type $R \begin{array}{c} \text{CR} \\ \diagup \quad \diagdown \\ \text{O} \end{array} \text{CH}$, the mean values of the specific exaltations are $E\Sigma_a + 0.67$, $E\Sigma_b + 0.72$, $E\Sigma_g - \Sigma_a + 37\%$ and $E\Sigma_v - \Sigma_a + 40\%$ (A., 1915, ii, 297), and for those of the type $R \begin{array}{c} \text{CR} \\ \diagup \quad \diagdown \\ \text{O} \end{array} \text{CR}'$, $E\Sigma_a + 0.87$, $E\Sigma_b + 0.92$, $E\Sigma_g - \Sigma_a + 46\%$ and $E\Sigma_v - \Sigma_a + 51\%$. In both cases R' may be alkyl or alkyloxy-groups. When the constants of the coumaranones are calculated on the assumption that these are hydroxycoumaranones, the mean values are $E\Sigma_a + 0.74$, $E\Sigma_b + 0.83$, $E\Sigma_g - \Sigma_a + 70\%$ and $E\Sigma_v - \Sigma_a + 82\%$. The exaltations of the refractions agree with those of the coumaranones, but not those of the dispersions.

Coumaranones of the type $R \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{O} \end{array} \text{CR}'R''$ must be ketonic. The constants for such are $E\Sigma_a + 1.31$, $E\Sigma_b + 1.41$, $E\Sigma_g - \Sigma_a + 89\%$ and $E\Sigma_v - \Sigma_a + 105\%$. The mean values of coumaranones which are capable of enolisation, calculated for the ketonic formula, are $E\Sigma_a + 1.37$, $E\Sigma_b + 1.48$, $E\Sigma_g - \Sigma_a + 86\%$ and $E\Sigma_v - \Sigma_a + 97\%$, values which agree with those of the preceding coumaranones. The optical evidence shows, therefore, that all coumaranones as yet examined are ketonic and not enolic in structure. It is also shown spectrochemically that the so-called coumaranonecarboxylic ester is really the enol, 2-hydroxycoumarilic ester, a result which confirms the chemical evidence (A., 1912, i, 1009).

It has been shown (Auwers, A., 1918, ii, 343) that 1-hydrindones and 1-ketotetrahydronaphthalenes exhibit higher exaltations than the homologues of acetophenone structurally allied to them. A further example is presented by 6-methoxy-2-methyl-1-hydrindone (preceding abstract) when compared with 3-methoxyacetophenone. The same phenomenon is seen with heterocyclic ketones containing two ring systems, such as the coumaranones and the chromanones. However, when the carbonyl group in a bicyclic ketone is not attached to the aromatic nucleus, no conjugation occurs, and such substances should be optically normal. This is practically the case with 2-hydrindone and the lactone of *o*-hydroxyphenylacetic acid, for which the values $E\Sigma_a + 0.40$ and $+0.10$, $E\Sigma_b + 0.42$ and 0.11 , $E\Sigma_g - \Sigma_a + 14\%$ and $+13\%$, and $E\Sigma_v - \Sigma_a -$ and $+11\%$ respectively are recorded.

C. S.

Guvacine. K. HESS and F. LEIBRANDT (*Ber.*, 1919, **52**, [B], 206—212. Compare A., 1918, i, 401—403).—In the earlier paper, guvacine was said to be demethylated arecaine, and dihydro-guvacine to be identical with *isonipecotinic* acid. Freudenberg, on the other hand (*ibid.*), claimed that guvacine is demethylated arecaine, which would make dihydroguvacine identical with

nipecotinic acid. Hess now agrees with Freudenberg, and with Winterstein and Weinlagen (this vol., i, 171). The discrepancy was due to the properties of *isonipecotinic* acid and dihydroguvacine not being sufficiently well established, and to the fact that a specimen of supposed nipecotinic acid obtained from technical " α -picoline" proved, after all, to be *isonipecotinic* acid.

Guvacine is therefore 1:2:5:6-tetrahydropyridine-3-carboxylic acid, guvacoline is its methyl ester, arecaine its 1-methyl derivative, and arecoline the methyl ester of this, whilst arecaine is to be cancelled.

The statement in the earlier paper that methylguvacine gives the ethyl ester of guvacine when boiled with alcoholic hydrogen chloride is also in need of correction. The ester arose from unmethylated guvacine, and the ethyl ester of methylguvacine was left in the residue from the distillation.

The following table gives the corrected data for the decomposition temperatures of dihydroguvacine (from guvacine regenerated from guvacoline), nipecotinic acid (Ladenburg), and *isonipecotinic* acid, and their hydrochlorides, platinichlorides, and aurichlorides:

| | Acid. | HCl. | Pt. | Au. |
|--------------------------------|-----------------------------|----------|----------|---------------------------------|
| <i>iso</i> Nipecotinic acid... | 328° (1H ₂ O) | 280° | 245° | 213—214° (1H ₂ O) |
| Nipecotinic acid | 249—250° | 239—240° | 212—213° | 195—197° |
| Dihydroguvacine ... | 252° | 232—234° | 235° | 195° |

J. C. W.

The Mobility of Hydrogen Atoms in Organic Molecules. Action of Phenylhydrazine on Dioxindoles. J. MARTINET

(*Compt. rend.*, 1919, 168, 689—691).—Dioxindole and five of its homologues, when acted on by phenylhydrazine, all gave phenylhydrazones of the type of the annexed formula, one molecule of the phenylhydrazine acting as an oxidising agent and the other combining to give the hydrazone.

Thus, in all these cases, a hydrogen atom attached to a carbon atom which was joined to a second carbon atom carrying a double linking was mobile.

W. G.

New Isomerism of the Isatogens. PAUL RUGGLI (*Ber.*, 1919, 52, [B], 1—8).—It is customary at present to represent isatogens by a quinonoid formula, $C_6H_4 \begin{smallmatrix} \text{C}(\text{O}) \\ \text{N}(\text{O}) \end{smallmatrix} \text{CR}$. By heating certain intensely coloured isatogens with alcoholic hydrogen chloride under pressure, the author has obtained less intensely coloured isomerides, for which there appears to be no formula possible except Baeyer's original formula for isatogens, namely, $O \begin{smallmatrix} \text{N}-C_6H_4 \\ \text{CR} \cdot \text{CO} \end{smallmatrix}$. This formula accords well with the properties of the new isomerides. Thus 6-nitro-2-phenylisatogen, $NO_2 \cdot C_6H_3 \begin{smallmatrix} \text{CO} \\ \text{NO} \end{smallmatrix} \text{CPh}$, is converted into

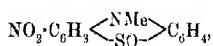
the *isomeride*, $\text{O} \begin{smallmatrix} \text{N}-\text{C}_6\text{H}_5 \cdot \text{NO}_2 \\ \text{CPh} \cdot \text{CO} \end{smallmatrix}$, pale yellow needles, m. p.

151–152°, which remains unchanged in pyridine solution after prolonged exposure to sunlight, forms an *oxime*, $\text{C}_{14}\text{H}_9\text{O}_4\text{N}_3$, yellow crystals, m. p. 180–181° (decomp.), and differs from 2:4-dinitrotolan in being saturated and in being precipitated unchanged by the addition of water to its solution in concentrated sulphuric acid.

Similarly, quinonoid ethyl 2-phenylisatogen-6-carboxylate is converted into an *isomeride*, faintly yellow needles, m. p. 100.5–101.5°, and methyl isatogenate is converted by methylalcoholic hydrogen chloride at the ordinary temperature into an *isomeride*, citron-yellow needles, m. p. about 165° (decomp., beginning at about 150°). The latter *isomeride* in acetone solution containing sodium iodide yields no iodine by acidification, whereas the corresponding quinonoid ester produces a considerable quantity by similar treatment. C. S.

Amino-derivatives of *N*-Methylphenazthionium. F. KEHRMANN and PAULINE ZYBS (*Ber.*, 1919, **52**, [B], 130–141).—The two series of salts of *N*-methylphenazthionium correspond optically with those of phenazthionium, but are considerably less stable (Kehrmann and Sandoz, A., 1918, i, 126). Since it is known that the introduction of electropositive groups, such as alkyl and amino-groups, into the chromogens of “onium” dyes renders the salts more stable towards water, amino-derivatives of *N*-methylphenazthionium have been prepared. The salts, however, are less stable than was anticipated.

3-Nitro-*N*-methylthiodiphenylamine *S*-oxide,

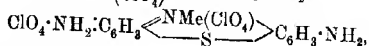


citron-yellow crystals, m. p. 177°, is obtained by the action of the strongest nitric acid in glacial acetic acid on *N*-methylthiodiphenylamine with cooling and the subsequent addition of water. By using twice the quantity of nitric acid, 3:6-dinitro-*N*-methylthiodiphenylamine *S*-oxide, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{NMe} \\ \text{SO} \end{smallmatrix} \text{C}_6\text{H}_3 \cdot \text{NO}_2$, is obtained,

pale yellow prisms, darkening at 280° and decomposing without melting at a higher temperature. The position of the nitro-groups in the *para*-positions to the nitrogen atom is proved by the identity of these nitro-derivatives with the products of the methylation of 3-nitro- and of 3:6-dinitro-thiodiphenylamine *S*-oxide (unpublished observations with Schmajewski). By reduction in alcoholic suspension with stannous chloride and hydrochloric acid, the mono-nitro-derivative yields the colourless staunichloride, and ultimately the *hydrochloride* of 3-amino-*N*-methylthiodiphenylamine, which is extremely unstable on account of its tendency to oxidise. By acetylation with sodium acetate and boiling acetic anhydride, the *hydrochloride* yields 3-acetyl-amino-*N*-methylthiodiphenylamine,

$\text{NHAc} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{NMe} \\ \text{S} \end{smallmatrix} \text{C}_6\text{H}_4$, colourless needles, m. p. 169° . The acetyl derivative in glacial acetic acid solution is converted by aqueous sodium nitrite into 3-acetylamino-N-methylthiodiphenylamine S-oxide, $\text{NHAc} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{NMe} \\ \text{SO} \end{smallmatrix} \text{C}_6\text{H}_4$, colourless crystals, decomp. about 235° , and by concentrated aqueous ferric chloride into the ferrichloride, black needles, of the meriquinonoid dye, which is converted by perchloric acid solution into the perchlorate, $\text{C}_{20}\text{H}_{28}\text{O}_{10}\text{N}_4\text{Cl}_2\text{S}_2$, bluish-black needles. When 3-acetylamino-N-methylthiodiphenylamine is boiled with 50% sulphuric acid, a cherry-red solution of the meriquinonoid sulphate of the acetylated base is obtained. This becomes orange as the acetyl group is hydrolysed, and ultimately olive-green when the solution is treated with hydrogen peroxide and concentrated sulphuric acid. The olive-green colour of the di-acid salt of the holoquinonoid dye remains at first unchanged after diluting the solution with ice-water, but rapidly becomes dirty blue as the salt hydrolyses.

A similar series of compounds is obtained from 3:6-dinitro-N-methylthiodiphenylamine S-oxide, namely, 3:6-diamino-N-methylthiodiphenylamine dihydrochloride, unstable, colourless needles, and its quinonoid oxidation product, which is isolated as the diperchlorate, $\text{NH}_2 \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{NMe}(\text{ClO}_4) \\ \text{S}(\text{ClO}_4) \end{smallmatrix} \text{C}_6\text{H}_3 \cdot \text{NH}_2$ or



violet leaflets with copper lustre (this salt is not hydrolysed by water), 3:6-diacetylamino-N-methylthiodiphenylamine, colourless needles, m. p. 265° , and 3:6-diacetylamino-N-methylthiodiphenylamine S-oxide, almost colourless crystals, decomp. about 270° .

C. S.

3:2'-Diquinolyl-2-carboxylic Acid. K. VON IHNATOWICZ and ST. VON NIEMENTOWSKI (*Ber.*, 1919, 52, [B], 186–188).—2-Cyanobenzoyl-1:2-dihydro-3:2'-diquinolyl, $\text{CN} \cdot \text{C}_6\text{H}_4 \cdot \text{BzN} \cdot \text{C}_6\text{H}_4 \cdot \text{N}$, honey-yellow crystals, m. p. 210° , is obtained by adding benzoyl chloride to a suspension of 3:2'-diquinolyl in aqueous potassium cyanide solution (compare Reissert, A., 1905, i, 472, 925). When left with concentrated hydrochloric acid for twenty-four to forty-eight hours, it is hydrolysed, and, after neutralisation with sodium hydroxide, yields 3:2'-diquinolyl-3-carboxylic acid, $\text{C}_{19}\text{H}_{15}\text{O}_3\text{N}_2$, microscopic plates of rhombic habit, m. p. 192° (decomp.), which forms a sheer salt, exhibits also basic properties, and is converted into 3:2'-diquinolyl by heating.

C. S.

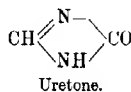
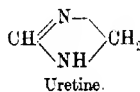
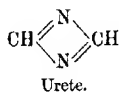
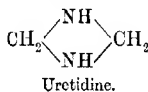
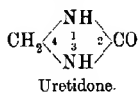
Syntheses of 8:8'-Dihydroxy-5:5'-diquinolyl and a Case of Direct Chlorination by means of Ferric Chloride. L. T. BATZ and ST. VON NIEMENTOWSKI (*Ber.*, 1919, 52, [B], 189–194).—When a solution of 8-hydroxyquinoline in about 3% hydrochloric acid is boiled with ferric chloride solution (80 grams in 200 grams of water) for two hours, and then basified with sodium hydroxide

solution and the black precipitate boiled with concentrated aqueous sodium hydroxide, the alkaline solution contains as the chief product of the reaction 5:7-dichloro-8-hydroxyquinoline, the by-products being 5-chloro-8-hydroxyquinoline and the dihydroxy-diquinolyl described below.

When a 0.3% aqueous solution of 8-hydroxyquinoline at about 40° is treated with ferric chloride solution (35 grams in 100 grams of water), and is then treated as above, 8:8'-*dihydroxy-5:5'-diquinolyl* is obtained in considerable quantity, together with chlorinated products. The formation of the latter is avoided by using ferric sulphate in place of ferric chloride. The dihydroxy-diquinolyl, $C_{18}H_{12}O_2N_2$, forms brownish-yellow crystals, m. p. 320—322°, softening at 310°. It is soluble in dilute mineral acids and alkalis, forms a *hydrochloride*, $C_{18}H_{12}O_2N_2 \cdot 2HCl \cdot 2H_2O$, yellow crystals, and *diacetyl* derivative, crystals, m. p. 187°, softening at 180°, and has been prepared from 3:3'-diamino-4:4'-dihydroxydiphenyl by the Skraup reaction. C. S.

Four-membered Cyclic Ureas. I. History and Nomenclature. WILLIAM J. HALE (*J. Amer. Chem. Soc.*, 1919, **41**, 370—378).—In 1869, Schiff obtained condensation products of urea with certain aldehydes, to which he assigned structures based on the ring system, $-N \langle \underset{O}{C} \rangle N-$. Since that time, Schiff's theory has been practically abandoned (see, especially, Dixon's work on the formaldehyde reaction, *T.*, 1918, **113**, 238), but other compounds have been discovered which unquestionably contain this heterocyclic system (see Fromm, A., 1893, i, 575; 1906, i, 656; 1913, i, 207; Frerichs and Hartwig, A., 1906, i, 74, 163; Senier and Shephard, T., 1909, **95**, 504).

In the further development of the subject which the author contemplates, a proper system of nomenclature for these four-membered ring compounds is desirable. Names with the root "diaz-" would be rational, but in recognition of Fromm's work as the pioneer, and of his terms "alduret" and "keturet," the following arrangement is adopted:



J. C. W.

Four-membered Cyclic Ureas. II. Condensation of isoCyanic Acid with a Schiff Base. WILLIAM J. HALE and NORBERT A. LANGE (*J. Amer. Chem. Soc.*, 1919, **41**, 379—388).—When finely powdered potassium cyanate is stirred into a cold

concentrated solution of benzaldazine in glacial acetic acid and the solution is left in a vacuum desiccator over soda-lime for a few days at 0°, 1:4-diphengluretidone, $\text{CHPh} \begin{smallmatrix} \text{NPh} \\ \text{NH} \end{smallmatrix} \text{CO}$, slowly separates in slender needles, m. p. 224–225° (decomp.) (compare the result obtained by Bailey and Moore under other conditions, A., 1917, i, 355). The compound forms a 3-acetyl derivative, m. p. 237°, and yields benzaldehyde and phenylcarbamide on hydrolysis. It cannot, however, be obtained by the condensation of these two substances. If warmed together or mixed with a little alcohol and a few drops of sulphuric acid, they yield *benzylidenebisphenylcarbamide*, $\text{CHPh}(\text{NH}\cdot\text{CO}\cdot\text{NHPH})_2$, m. p. 198–199° (decomp.), whilst condensation with alcoholic hydrogen chloride furnishes the *hydrochloride of phenyl- α -ethoxybenzylcarbamide*, which is hydrolysed to the free base, $\text{NHPH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CHPh}\cdot\text{OEt}$, an amorphous substance, softening at 150–155°, when its alcoholic solution is poured into water.

Benzylidene-ethylamine reacts with isocyanic acid in quite a different manner; no crystals separate, but if the acetic acid is removed by a current of steam, 4:6-diketophenyl-1-ethylthexahydro-1:3:5-triazine, $\text{CHPh} \begin{smallmatrix} \text{N} \cdot \text{CO} \\ \text{NH} \cdot \text{CO} \end{smallmatrix} \text{NH}$, may be isolated in clusters of needles, m. p. 226°.

Staudinger has already directed attention to the similarity between carbimides and ketens with respect to their reactions with unsaturated compounds (A., 1917, i, 666), and it is noteworthy that he has found the same kind of divergence between benzylidene derivatives of aromatic and aliphatic amines as that illustrated above (A., 1910, i, 586).

J. C. W.

Diacetylingidotin. D. VORLÄNDER and JOHANNES VON PFEIFFER (*Ber.*, 1919, 52, [B], 325–329).—Proof is adduced that the acetyl groups in diacetylingidotin are attached to nitrogen, which helps to explain why the compound differs so widely from indigotin in colour.

Indoxyl acid, prepared by fusing the sodium salt of phenylglycine-*o*-carboxylic acid with sodium hydroxide, is heated with acetic anhydride at 90–100°, and thus converted into *N*-acetyl-indoxyl (A., 1901, i, 563). The position of the acetyl group follows from the fact that acetylanthranilic acid is formed if the compound is boiled with an excess of potassium permanganate in acetone. Diacetylingidotin is formed immediately, and it can be prepared conveniently in this way if an excess of permanganate is avoided. It crystallises from benzene in red prisms or pyramids, m. p. 245–250°, and yields a comparatively soluble form of indigotin when boiled with an acetic acid solution of hydrogen chloride.

O-Acetylindoxyl (*ibid.*) yields indirubin when oxidised by perhydrol in acetic acid solution.

Although indoxyl yields the two acetyl derivatives, indigo-white

only yields one diacetyl derivative. This is the *N*-isomeride, for it may be oxidised to acetylanthranilic acid.

Diacetyl-o-dimethylindigo-white, $C_{20}H_{20}O_4N_2$, obtained by acetylating the alkaline solution of "*o*-tolylindigo-white," crystallises in white tablets, m. p. 245–248°, and may be oxidised by nitrogen trioxide fumes to *diacetyl-o-dimethylindigotin*, orange-yellow tablets, m. p. 178° (decomp.). The corresponding *dibenzoyl* compound forms yellow crystals, m. p. 175° (decomp.). J. C. W.

Mercury Mercaptide Nitrites and their Reaction with the Alkyl Iodides. IV. Chain Compounds of Sulphur (*continued*). PRAFULLA CHANDRA RAY and PRAFULLA CHANDRA GUHA (T., 1919, 115, 261–271).

Dihydroxydihydroglyoxalines and their Conversion into Glyoxalines. II. OTTO DIELS and CARRY SALOMON (*Ber.*, 1919, 52, [B], 43–51. Compare Diels, A., 1918, i, 448).—Further experiments have been undertaken to characterise and to confirm the constitution of 3:4-oxido-2-phenyl-4:5-dimethyl-3:4-dihydroglyoxaline (*loc. cit.*). It reacts additively with acetyl chloride to form a compound, $C_{13}H_{13}O_2N_2Cl$, colourless crystals, m. p. 143°, with benzoyl chloride to form the compound, $C_{18}H_{17}O_2N_2Cl$, crystals, m. p. 162°, both of which are stable, with phenylcarbimide in pyridine solution to form the compound, $C_{18}H_{17}O_2N_3$, colourless crystals, m. p. 140°, and with ethylcarbimide in benzene solution to form the compound, $C_{14}H_{17}O_2N_3$, crystals, m. p. 116–118°. It is converted into 2-phenyl-4:5-dimethylglyoxaline by anhydrous ethylamine in benzene solution at 160°, or more smoothly by phenylhydrazine at 200–210°. C. S.

peri-Naphthylenediamine and Selenious Acid. O. HINSBERG (*Ber.*, 1919, 52, [B], 21–28).—The reaction studied by Sachs (A., 1909, i, 426) has been more thoroughly examined. *peri*-Naphthylenediamine (2 mols.) dissolved in pyridine is treated with a solution of selenious acid (1 mol.) in aqueous pyridine, whereby *dihydrodi-peri-naphthaselenendiazole*, $C_{10}H_6 \begin{smallmatrix} <NH \\ <NH \end{smallmatrix} Se \begin{smallmatrix} <NH \\ <NH \end{smallmatrix} C_{10}H_6$ is obtained after the addition of water. It forms yellowish-red flocks, m. p. 120°, and is oxidised very easily, even by air, to *di-peri-naphthaselenendiazole*, $C_{10}H_6 \begin{smallmatrix} <N \\ <NH \end{smallmatrix} Se \begin{smallmatrix} <NH \\ <N \end{smallmatrix} C_{10}H_6$, brown, crystalline powder, m. p. above 300°, which is very sparingly soluble in all solvents except pyridine (*hydrochloride*, blackish-violet needles). *Di-peri-naphthaselenendiazole* is decomposed by zinc dust, glacial acetic and concentrated hydrochloric acids on the water-bath, yielding hydrogen selenide and 1:8-naphthylenediamine, and is oxidised by ferric chloride and hydrochloric acid, yielding a black powder, decomp. above 300°, the nature of which has not been ascertained, but it is probably identical with the product obtained from equal molecular quantities of selenic acid and

1:8-naphthylenediamine by warming in dilute acetic acid solution on the water-bath.

The bearing of the preceding results on the author's theory of the structure of the selenium atom (A., 1918, ii, 106) is discussed.

C. S.

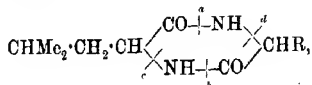
Distillation of Egg Albumin under Reduced Pressure.

AMÉ PICTET and MARC CRAMER (*Helv. Chim. Acta*, 1919, 2, 188—195).—The tar obtained by the dry distillation of animal matter contains substances like aniline, pyridine, and quinoline which bear no relationship to the amino-acids of the proteins. The question arises, therefore, whether the protein complexes contain such atomic groupings, hitherto unrecognised, or whether these compounds are formed by the pyrogenic transformations or condensations of the primary decomposition products. In the hope of throwing some light on the problem, the authors have distilled 4 kilos. of egg-albumin under a pressure of 20—22 mm., but with little success.

Up to 70°, the only product is water; at about 150°, a brisk evolution of gas commences, mostly soluble in sodium hydroxide or dilute sulphuric acid; towards 220°, a yellow oil begins to distil, but at 350° distillation ceases, a very porous and light coke being left behind. The relative proportions of the products are as follows: water, 30%; organic compounds dissolved in this water, 6%; insoluble oil, 9%; coke, 32%; gas and losses, 23%.

The organic compounds are entirely soluble in ether, and can be differentiated into acidic, basic, and neutral fractions. Acetic, propionic, *n*-butyric, and succinic acids may be detected in the first fraction, but no aromatic acids. The bulk of the bases distils at about 175°, and appears to consist of a single primary amine of the formula C_6H_9N . It is a very mobile oil, which does not form a diazonium salt, but liberates benzene and nitrogen when warmed with nitrous acid. It is suggested, therefore, that the base may be a dihydroaniline of the formula $NH_2 \cdot CH < \begin{smallmatrix} CH_2 \cdot CH \\ CH = CH \end{smallmatrix} > CH$. It forms a *picrate*, m. p. 185°, and may be acetylated or benzoylated. Pyrrolic bases of higher boiling points are also present.

The chief product of the distillation is found among the neutral substances. It is *isohexoamide*, $CHMe_2 \cdot CH_2 \cdot CH_2 \cdot CO \cdot NH_2$, m. p. 120°. The isolation of this amide has important consequences, since it throws light on the origin of the *isohexonitrile*, which is one of the principal constituents of animal oil (Weidel and Ciamician, A., 1880, 403), and also links this nitrile with leucine, the main product of hydrolytic cleavage, in a common stock, namely, a diketopiperazine ring substituted by an *isobutyl* radicle. Thus, in the formula



cleavage at *a* and *b* results in the formation of leucine, and at *c* and *d* in the production of isohexoamide. The neutral fraction contains other amides of fatty acids and compounds of the indole series, including indole itself, which has not been reported in animal oil.

It was expected that the aqueous portion of the distillate would contain lavoglucosan if egg-albumin contains a glucose grouping, but no trace of the substance could be detected. J. C. W.

Compressibility of Aqueous Solutions of Casein and Peptone. SVEN PALITZSCH (*J. Amer. Chem. Soc.*, 1919, **41**, 346—351, and *Compt. rend. Lab. Carlsberg*, 1919, **14**, 14—20).—The compressibility, hydrogen-ion concentration, viscosity, specific volume, and density of acid casein solutions, alkaline casein solutions, and peptone solutions have been measured for a series of concentrations at 20°. The compressibilities were measured over the range 100—300 megabars. The compressibility of casein solutions decreases with rising concentrations, and very nearly to the same extent in weakly acid and in weakly alkaline solutions. The compressibility of peptone solutions also decreases, even more markedly, with rising concentration. For the concentration of 10 grams in 100 grams of water, the compressibility of acid casein solution is 40.6×10^{-6} , of alkaline casein solution 40.5×10^{-6} , and of a peptone solution 39.0×10^{-6} . J. F. S.

Nuclein Metabolism. VI. The Cleavage of Nucleotides by means of Hot Aqueous Picric Acid Solutions. Isolation of Crystalline Cytidine-phosphoric Acid. S. J. THANNHAUSER and G. DORFMÜLLER (*Zeitsch. physiol. Chem.*, 1919, **104**, 65—72).—The triphosphonucleic acid obtained from yeast-nucleic acid by hydrolysis with ammonia was further hydrolysed by treatment with hot picric acid solution. From the reaction mixture, a crystalline, brucine salt of cytidine-phosphoric acid was isolated,

$C_9H_{14}O_8N_8P(C_{28}H_{26}O_4N_2)_2$,
m. p. 180—182°. This yielded the free cytidine-phosphoric acid, $C_9H_{14}O_8N_8P$, in a crystalline condition, monoclinic-sphenoidal crystals, m. p. 227°, $[\alpha]_D^{20} = +23.43^\circ$. The two triphosphonucleic acids previously described (*A.*, 1918, i, 47) were submitted to the picric acid hydrolysis. Both yielded the brucine salt of cytidine-phosphoric acid, but only from the *l*-triphosphonucleic acid, m. p. 205°, was the free cytidine-phosphoric acid isolated in the crystalline condition. The inactive triphosphonucleic acid, m. p. 185—187°, is therefore not regarded as a pure substance.

A mixture of uridine-phosphoric acid and cytidine-phosphoric acid may be obtained by hydrolysis of yeast-nucleic acid with picric acid, and the two products may be separated by careful fractional recrystallisation of their brucine salts. J. C. D.

Absorption of Water by Gelatin. EDITH B. SHREVE (*J. Franklin Inst.*, 1919, **187**, 319—337).—The amount of water

absorbed by a gelatin jelly invariably increases with rise of temperature. Since the absorption is accompanied by development of heat, and contraction, Le Chatelier's theorem would require a decreasing water absorption for increasing temperature; it is suggested that the apparent discrepancy is due to the very slow rate of the reaction, equilibrium not being reached before decomposition of the gelatin begins. Hofmeister's results are confirmed, the amount of absorption in some salt and other solutions being less than in water, but greater in other solutions; if, however, the jellies are made up with these solutions instead of with water, the amount of water absorption is in all cases greater than for a jelly made with water only. The bearing of this result on biological conclusions drawn from imbibition experiments is discussed. [See also *J. Soc. Chem. Ind.*, 1919, 297A.]

B. V. S.

The Influence of Saponin on the Action of Lipases. A. L. FLOHR (*Arch. Néerland. physiol.*, 1919, 3, 182—189).—Solutions of saponin activate pancreatic lipase, the influence exerted increasing with the concentration of the saponin up to 2% and then decreasing, using equal volumes of oil and saponin solution. The curves showing these results are analogous to those representing the variation of surface tension of saponin solutions with concentration.

On the other hand, saponin exerts an inhibiting action on the lipase of ricin, the influence increasing steadily with the concentration of the saponin.

W. G.

Preparation of Primary and Secondary Arsanilic Acids.

PHILIP ADOLPH KOBER and WALTER S. DAVIS (*J. Amer. Chem. Soc.*, 1919, 41, 451—458).—The preparation of the so-called primary arsanilic acid was first described by Béchamp in 1863, but the details of the processes which are in use on the large scale, are comparatively secret. The authors have now discovered a simple method for making either the primary or secondary arsanilic acid in a pure state (compare this vol., i, 182).

p-Aminophenylarsinic Acid.—1000 C.c. of technical arsenic acid (76%) are concentrated to 100% by heating at 120—140° for twelve or fifteen hours, then cooled, and stirred into 1400 c.c. of dry, ice-cold aniline. The arsenate so formed (aniline: acid, 3:2) is ground to a powder, and then 200 grams of it are stirred at 160° until solten, and finally heated under reflux for one to one and a-half hours at 160—170° and for one hour at 180—185°. After cooling somewhat, 225 c.c. of 6*N*-sodium hydroxide and 225 c.c. of water are added, when the unchanged aniline is run off and the aqueous layer is shaken with kaolin or kieselguhr, and filtered. The clear solution is mixed with 100 c.c. of 6*N*-hydrochloric acid, and then small portions are tested to see how much more acid is required to cause the complete precipitation of the arsanilic acid. When this has been added, the almost solid mass is filtered, washed by suspending it in 200 c.c. of water, and filtered again.

Di-p-aminophenylarsinic acid, $\text{OH}\cdot\text{AsO}(\text{C}_6\text{H}_4\cdot\text{NH}_2)_2$.—56.4 C.c. of commercial arsenic acid and 1500 c.c. of aniline are heated at 230° in a flask fitted with an inlet tube reaching to the bottom and a condenser, a current of air being drawn through the liquid to ensure good mixing. When about 1200 c.c. of aniline have distilled over, the product is cooled, shaken with 3*N*-sodium hydroxide, and the aqueous layer is then agitated with infusorial earth and filtered. The solution is acidified by 3*N*-acetic acid, and the crude *sec*-arsanilic acid which separates is purified by dissolving in 3*N*-alkali, removing any aniline by a current of steam, and then adding acetic acid, first until a small precipitate of coloured products is formed, and finally until the acid is completely reprecipitated. J. C. W.

Preparation of Sodium *p*-Hydroxyphenylarsinate. JAMES B. CONANT (*J. Amer. Chem. Soc.*, 1919, **41**, 431–435).—The preparation of *p*-hydroxyphenylarsinic acid from phenol and arsenic acid represents a first stage in the synthesis of “salvarsan,” but little has been published about the reaction beyond the notes of the German patent (A., 1909, i, 279). It is now stated that the best results, giving a yield of about 21.5%, are obtained by heating a well-stirred mixture of phenol and a syrupy arsenic acid corresponding with the formula H_3AsO_4 , at 147 – 157° , for three hours. An excess of acid is used amounting to 10% of the theoretical requirement, and practically nothing but a small quantity of water is lost during the process. The isolation of the sodium salt of the product is best performed as follows. The aqueous solution of the crude acid is filtered from tar, mixed with barium hydroxide until the brown colour begins to change to pink, and then extracted several times with ether to remove tarry matter. More barium hydroxide is then added until a test portion, after rendering it alkaline and filtering, shows the presence of barium ions, when the solution is made just alkaline by the addition of sodium hydroxide, and filtered. The excess of barium is removed by sodium sulphate, and the filtrate evaporated to a red syrup. Impurities are now finally removed by adding sulphuric acid until the colour becomes yellow, when they separate as a viscous, brown oil. The clear solution is then neutralised again and evaporated, a mixture of sodium sulphate and *p*-hydroxyphenylarsinate being obtained. If desired, the latter salt can be extracted by means of alcohol and crystallised.

The next step in the synthesis of “salvarsan” is the nitration of the *p*-hydroxyphenylarsinic acid. For this purpose, the above mixture of sodium salts is quite suitable, but it must be roughly analysed before use. This can be done by taking advantage of the fact that the arsenic acid is converted into tribromophenol on the addition of bromine water. In the nitration, the crude salt, dried at 100° , is stirred into about half its weight of sulphuric acid at 0° , and the nitrating mixture, containing one equivalent of nitric acid, is slowly added. The temperature is allowed to rise gradu-

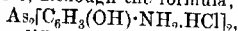
ally to 10°, when the mixture is diluted and the nitro-compound filtered next day.

J. C. W.

Arsenical Compounds. WALTER A. JACOBS, WADE H. BROWN, MICHAEL HEIDELBERGER, and LOUISE PEARCE (Amer. Pats. 1280119—1280223 and 1280225—1280227).—Several derivatives of *N*-phenylglycine-*p*-arsinic acid are described in which the aromatic nucleus containing the arsenic radicle is connected with the α -amino-group of an α -aminoacylamino-side-chain. These compounds are powerful agents in the treatment of trypanosomal and spirochaetal infections. The general methods of preparation consist in treating the sodium salt of *p*-aminophenylarsinic acid with amides, ureides, or anilides of halogenacetic acids, or by treating the methyl ester of *N*-phenylglycine-*p*-arsinic acid with an amine. U.S. Pat. 1280119 relates to amides of *N*-phenylglycine-*p*-arsinic acid or substituted derivatives of the general formula $\text{-NH}\cdot\text{CHR}\cdot\text{CO}\cdot\text{NR}'\text{R}''$, where R is alkyl, aryl, or hydrogen, and R' and R'' are alkyl or hydrogen. 1280120 relates to *N*-phenylglycine- β -methylureide-*p*-arsinic acid, or generally to derivatives having the side-chain $\text{-NH}\cdot\text{CHR}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NR}'\text{H}$, in which R and R' are alkyl, aryl, or hydrogen. 1280122 relates to *m*'-amino-phenol-*N*-phenylglycine-*p*-arsinic acid, or generally to derivatives with the side-chain $\text{-NH}\cdot\text{CHR}\cdot\text{CO}\cdot\text{NHAr}$, in which R is alkyl, aryl, or hydrogen, and Ar is an aromatic radicle with or without substituted groups. 1280122 relates to arsenoxides containing the group -As=O , obtained by the action of mild reducing agents, such as sulphurous acid, on the amides and anilides specified above. 1280123 relates to arsenophenylglycinebisarylamides, obtained by the action of powerful reducing agents on the anilides specified above, whereby two molecules of the anilide unite together, by condensation and reduction, through the bond -As=As- . These are formed by the action of hypophosphorous and hydriodic acids on the corresponding arsenic acids or arsenoxides; they have a more powerful therapeutic effect than the arsenic acid derivatives. 1280125 relates to readily soluble sodium salts of the above ureides, 1280126 to readily soluble sodium salts of the above anilides, and 1280127 to readily soluble hydrochloric or other acid salts of the above arsenoaryl condensation derivatives, the salt-forming acid being attached to the α -amino-groups of the side-chains in the *para*-position to the arsenic.

J. F. B.

Preparation of Arsphenamine [Salvarsan]. PHILIP ADOLPH KOBER (*J. Amer. Chem. Soc.*, 1919, **41**, 442—451. Compare this vol., i. 183).—The percentage of arsenic in salvarsan is generally found to be about 31·6, although the formula,



requires 34·2%. The difference is usually ascribed to the presence of two molecules of water, although the drug, as prepared by Ehrlich and Berthelm's method (*A.*, 1912, i. 523), is actually precipitated by methyl alcohol and ether, and these authors have shown that it contains one molecule of methyl alcohol. Kober is

of the opinion that the serious fluctuations in the toxicity of the various preparations, about 50% of which have to be rejected, are largely due to the use of methyl alcohol and ether, and has therefore designed a method for preparing the drug in which no use of these physiologically dangerous and inflammable solvents is made.

A solution of 85 grams of crude nitrohydroxyphenylarsinic acid in 290 c.c. of 2*N*-sodium hydroxide and 1700 c.c. of water is stirred into a solution of 220 grams of magnesium chloride and 1100 grams of sodium hyposulphite in 5500 c.c. of water. The mixture is kept at below 40° until the small amount of suspended impurities seems to be about to settle, when it is rapidly filtered, and the solution kept at 50–60° for two hours or so until the diaminodihydroxy-arsenobenzene is deposited. The yellow base is washed with ice-cold water, suspended in 400 c.c. of water, and dissolved in 2*N*-sodium hydroxide, 150 c.c. being sufficient as a rule, all the liquids being cooled to 0°. The solution is then filtered through an anaerobic filter, mixed with 150 c.c. of hydrochloric acid (1:1), and then made up to 1700 c.c. The hydrochloride is finally "salted out" by slowly stirring the solution into 3250 c.c. of hydrochloric acid (1:1), and is dried in a vacuum desiccator over calcium chloride and sodium hydroxide.

Obtained in this way, salvarsan is a pale greyish-white powder containing 1 or 2H₂O, according to the drying, and charring at about 180°. It is less hygroscopic, and therefore more stable, than the ordinary preparations, and has a low grade of toxicity.

A summary of characteristic tests for salvarsan is given.

J. C. W.

Organo-chromium Compounds. F. HEIN (*Ber.*, 1919, 52, [B], 195–196).—By the action of magnesium phenyl bromide on anhydrous chromic chloride or chromyl chloride is obtained, together with other chromium phenyl compounds (as yet unexamined), an orange, amorphous substance which appears to be *chromium pentaphenyl bromide*, CrPh₅Br. It is not attacked by water, but is decomposed by acids, forms a *mercurichloride*, CrPh₅Br, HgCl₂, and has in boiling chloroform a molecular weight corresponding with its formula.

C. S.

Physiological Chemistry.

The Sugars of the Blood. J. W. BEST (*Arch. Néerland. physiol.*, 1919, 3, 222–266).—The blood of oxen and of horses, taken in the absence of digestion, contains 0.057–0.065% of dextrose, 0.002–0.005% of lactose, and <0.006–0.012% of an unknown sugar. Galactose, sucrose, melibiose, maltose, and isomaltose are

not present, or, if present, only in quantities less than 0.001%. The unknown sugar is formed by condensation from one or two molecules of a pentose, and contains about twelve atoms of carbon. It gives a phenylosazone, m. p. 181—182°, which from its crystalline form, solubility, and m. p. resembles the osazone of Cummidge's sugar (compare *Proc. Roy. Soc.*, 1909, **81**, 374). The sugar is not attacked by either *Saccharomyces cerevisiae*, or emulsin, or the yeast which ferments lactose. It is dextrorotatory. It is not hydrolysed by boiling with dilute mineral acids, or at least only very slowly. The sugar exists as such in the blood, and is not formed during the hydrolysis of the gum of the blood.

The blood of human beings taken in the morning, eleven to sixteen hours after the last meal, contains 0.047—0.082% of dextrose, the residual reduction being equal to 0.019—0.031%, of which half is due to substances precipitable by phosphotungstic acid. Of the remainder, about 0.013% is due to the presence of the unknown sugar described above. Examination of the phenylosazones from the blood sugars before and after fermentation indicates the presence of lactose in human blood, and in one case, that of a woman, thirty-six weeks in pregnancy, 0.006% was found.

W. G.

Hæmocyanin. ERNST PHILIPPI (*Zeitsch. physiol. Chem.*, 1919, **104**, 88—94).—Hæmocyanin is very sensitive to acids. Snails' blood is immediately decolorised by the addition of small quantities of oxalic acid. After treating snails' blood with potassium hydroxide, a product was isolated which contained 7.0% of copper and gave an intense pyrrole reaction. The presence of manganese in the blood of *Pinna squamosa* is confirmed.

J. C. D.

The Effect of Acetone and of β -Hydroxybutyric and Acetoacetic Acids on the Blood Catalase. W. E. BURGE (*J. Biol. Chem.*, 1919, **37**, 343—347).—Introduction of doses of 5 grams per kilo. of 30% solutions of acetone, acetoacetic acid, and β -hydroxybutyric acid into the upper part of the intestines of rabbits produced a rise in the catalase content of blood taken from the jugular vein. Measurements of the catalase present in blood taken from the liver and the portal and jugular veins before and after the administration of these substances in this manner indicate that they stimulate the liver to an increased output of the enzyme. The increased oxidation in diabetes is attributed to the increased production of catalase resulting from such stimulation of the liver.

J. C. D.

The Mechanism of the Action of Fats in the Utilisation and Assimilation of Proteins. F. MAIGNON (*Compt. rend.*, 1919, **168**, 626—629. Compare A., 1918, i, 416).—The author reasserts his views as to the part played by the fatty acids in the building up of specific proteins in the body from the amino-acids arising from the ingested proteins (compare this vol., i, 185).

W. G.

Growth. XI. The Growth, and Senescence of White Mice fed upon Pituitary (Anterior Lobe) Tissue, Tethelin, Egg Lecithin or Cholesterol. T. BRAILSFORD ROBERTSON and L. A. RAY (*J. Biol. Chem.*, 1919, **37**, 393—426).—The results previously reported (A., 1916, i, 350, 690) dealt with the influence of these substances on the growth of mice up to the sixtieth week of life. The present paper records extended observations which cover the whole life-period of the animals. Generally speaking, the results confirm the conclusions announced in the earlier reports. The substances administered to the animals influenced the growth process in the way that catalysts influence chemical reactions, that is, by affecting the velocity with which the equilibrium is attained without affecting the equilibrium itself. J. C. D.

Growth. XII. The Influence of Pituitary Gland (Anterior Lobe) Tissue, Tethelin, Egg Lecithin, and Cholesterol on the Duration of Life of the White Mouse. T. BRAILSFORD ROBERTSON and L. A. RAY (*J. Biol. Chem.*, 1919, **37**, 427—442).—The mean duration of life of mice which have received pituitary tissue, lecithin, or cholesterol lies within normal limits. Those which had received tethelin, the growth-accelerating substance isolated from the anterior lobe of the pituitary gland, showed a greatly extended duration of life. Male mice which had received tethelin continuously showed a duration of life which exceeded the normal by ninety-nine days, whilst in female mice which had received tethelin intermittently in three periods of one month each prior to the thirtieth week, the increased duration of life was eighty-one days. J. C. D.

Growth. XIV. Further Experiments on the Influence of Tethelin on the Growth of the White Mouse. T. BRAILSFORD ROBERTSON and L. A. RAY (*J. Biol. Chem.*, 1919, **37**, 455—463. Compare A., 1916, i, 356, 690).—Discontinuous administration of tethelin will produce the characteristic deformations of the growth curve of white mice. The same result was observed to follow a single relatively brief period of administration, namely, 4 mg. of tethelin per day for eight weeks only, from the fourth to the twelfth week of life. The concavity in the curve of growth is believed to be the expression of preliminary retardation preceding sexual maturity, followed by a secondary or compensatory acceleration accompanying and succeeding sexual maturity. The previous opinion, which held that both acceleration and retardation were directly due to tethelin, is now modified in that only the retardation is believed to be due to that substance, the acceleration being due to compensatory factors which develop in the animal itself in response to the abnormal dosage of the active principle of the anterior lobe of the pituitary body. The direct action of tethelin would thus appear to consist exclusively, so far as the whole animal is concerned, of retardation of growth. J. C. D.

Milk Coagulation and the Physical Condition of Milk Curd. O. ALLEMANN [with H. SCHMIDT] (*Kolloid Zeitsch.*, 1919, **24**, 27—42).—A number of experiments on the solidity of milk curds have been made in connexion with the manufacture of cheese. It is shown that the solidity of rennet curd is directly proportional to the time which has elapsed since coagulation, and inversely proportional to the time of coagulation. The solidity is proportional to the acidity of the mixture. The solidity of the milk curd is increased by the addition of potassium chloride in strict proportion to the amount of salt added. With increasing temperature, the solidity increases up to a maximum, but above 41—42° it decreases rapidly. The solidification of the curd is a continuation of the coagulation process, and it takes place according to the ordinary coagulation laws. The solidity is dependent on the individuality of the animal from which the milk was taken, and is constant over long periods of time. Sudden changes in the solidity relationships can occur; these are the result of weather changes and physiological conditions, and after a short time the solidity relationships return to their normal values.

J. F. S.

The Forms of Nitrogen in Protein-free Milk. CORNELIA KENNEDY (*J. Amer. Chem. Soc.*, 1919, **41**, 388—393).—The so-called protein-free milk is prepared as follows: 40 litres of centrifuged milk, diluted with 8 litres of water, are mixed with a little more than the required amount of hydrochloric acid to cause the formation of a curd, filtered through cheesecloth, the filtrate is boiled for half a minute, cooled, filtered through paper pulp, and the solution neutralised with sodium hydroxide and evaporated to dryness at 60—70°. An examination of the distribution of nitrogen in five samples of such milk, obtained from the same herd at different times, has been made, with the following results: (1) the nitrogenous substances present vary in composition; (2) considerable quantities of proteins or peptides of high molecular weight are still present, for there is a great increase in the amount of amino-nitrogen after hydrolysis or tryptic digestion; (3) nearly half of the nitrogenous material is precipitated by mercuric nitrate or phosphotungstic acid, the latter agent removing only non-amino-nitrogen.

J. C. W.

Action of 10 per cent. Thymol-Chloroform Preservative on the Chlorine Content of Urine. J. O. HALVERSON and J. A. SCHULZ (*J. Amer. Chem. Soc.*, 1919, **41**, 440—442).—A solution of thymol in chloroform is being widely used as a preservative for specimens of urine. Its influence on the content of inorganic chlorine has therefore been studied in the case of six alkaline specimens of cow's urine, stored at about freezing point for nearly two years, and sixteen specimens of acidic urine from swine, kept at the ordinary temperature for four to twenty-one days. No variations outside the limits of analytical errors were encountered.

J. C. W.

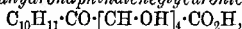
Cystine of Urine and of Urinary Calculi. EMIL ABDERHALDEN (*Zeitsch. physiol. Chem.*, 1919, **104**, 129—132. Compare A., 1907, i, 476).—The cystine derived from the hydrolysis of hair and nails of a cystinuric patient was found to be identical with that present in the urine. Three cystine calculi contained traces of tyrosine, but a fourth was composed exclusively of cystine. This cystine possessed the same properties as that derived from the keratins. J. C. D.

Hæmoquinic Acid. A New Disintegration Product of Quinine Present in the Urine, especially in "Blackwater" Fever. M. NIERENSTEIN (*J. Royal Army Med. Corps*, 1919, 215—217).—Occasionally, dark-coloured urines have been observed to follow the administration of quinine. These cases were examined for the presence of kynurenic acid, but without success. An extension of the method for the isolation of kynurenic acid led, however, to the isolation of a new disintegration product of quinine, *hæmoquinic acid*. The acid crystallised from dilute alcohol has m. p. 183° (decomp.). It may be recognised in dilutions as great as 1 in 5000 by means of the blue coloration given with Herapath's reagent. It yields a *picrate*, m. p. 224° , and a *sulphate* crystallising from water in small, silky needles. In addition to "blackwater" urines, the urines of the following malaria cases were also examined for this acid: (1) patients having quinine; (2) patients soon after rigor; (3) patients some time after rigor. The results of this study suggest a possible relationship between the formation of hæmoquinic acid in the organism and the production of "blackwater." Hæmoquinic acid shows pronounced hæmolytic properties towards human and sheep's corpuscles. It is possible that the acid is 6-methoxyquinoline-3-glyoxylic acid, $C_9NH_5Me \cdot CO \cdot CO_2H$. J. C. D.

Chitenine. A Disintegration Product of Quinine Found in the Urine. M. NIERENSTEIN (*J. Royal Army Med. Corps*, 1919, 218—219).—The observation of Kerner (*Arch. gesamt. Physiol.*, 1869, 200) that chitenine, an oxidation product of quinine, is found in the urine after the administration of quinine is confirmed. It is present in the urine in the early stages of the excretion of quinine. Chitenine was isolated from the urine of a normal individual collected during the first two or three hours after the administration of quinine sulphate by a fractionation of the precipitate produced on the addition of picric acid. The chitenine obtained from the urine crystallised from dilute alcohol in prisms, m. p. $281-282^{\circ}$. $[\alpha]_D^{25} -122.6^{\circ}$, and showed other properties similar to those of the chitenine described by Skraup (A., 1893, i, 737). J. C. D.

The Fate of Tetrahydronaphthalene (Tetralin) in the Animal Body. JULIUS POHL and MARGARETE RAWICZ (*Zeitsch. physiol. Chem.*, 1919, **104**, 95—104. Compare Schroeter and Thomas, A., 1918, i, 418).—Tetrahydronaphthalene is slightly

toxic, but rabbits weighing 2 kilos. can tolerate the administration of 2—3 grams by the stomach without showing apparent symptoms. Smaller animals develop diarrhoea and die, exhibiting narcosis. Tetrahydronaphthalene administered to the rabbit is excreted mainly as *ac-a-tetrahydronaphthaleneglycuronic acid*,



m. p. 256—258°, crystallising in colourless, lustrous plates. A small portion is excreted unchanged by the respiratory tract. When tetralin is administered orally to man, 5—7 grams per day, the urine is inactive, dark green, and readily yields an amorphous pigment. It also contains a leuco-compound, which is readily oxidised to a deep blue pigment, besides dihydronaphthalene and naphthalene. Dihydronaphthalene is chiefly excreted as the conjugated glycuronic acid, which readily yields naphthalene. Other substances isolated from the urines, such as *ac-a-tetrahydronaphthylcarbamide* and a substance melting at 286°, are regarded as products of secondary reactions. J. C. D.

Chemistry of Vegetable Physiology and Agriculture.

Nitrate and Nitrite Assimilation. XIV. Iron and Oxygen as Necessary Agents for the Reduction of Alkali Nitrites by Auto-oxidisable Compounds. OSKAR BAUDISCH (*Ber.*, 1919, 52, [B], 35—40. Compare A., 1918, i, 474).—An explanation has now been found of the fact that iron as well as oxygen is necessary for the reduction. It has been shown (*loc. cit.*) that tervalent iron must be present in a complex form in order to produce nitric oxide or ammonia from an alkali nitrite. It is now shown that when an aqueous alkaline solution of sodium nitroprusside is boiled in the absence of air or oxygen, no nitric oxide is liberated, and that this gas is produced in large quantity directly oxygen is admitted to the system. A similar result is obtained by heating a solution of sodium carbonate and potassium nitrite with sodium ferri-pentacyanoammine, $[(\text{CN})_5\text{FeNH}_2]\text{Na}_3$, in the presence of oxygen. The whole process of the reduction of alkali nitrite is, therefore, a replacement of inorganic or organic groups co-ordinatively attached to the iron atom by the NO-group of the alkali nitrite, and the subsequent elimination of this group by oxygen on warming. In accordance with this, nitrous acid is found in the distillate when a solution of potassium ferrocyanide is boiled with sodium carbonate and sodium nitrite in the presence of oxygen. The elimination of the cyano-group, however, occurs only very slowly, so that only slight traces of nitric oxide are formed, but this gas is liberated in considerable quantity when a little pyridine is added to the reaction mixture. The pyridine may be replaced by phloroglucinol.

Contrary to previous statements, it is not necessary that the compound capable of entering into complex salt formation with the iron must be auto-oxidisable in order to reduce alkali nitrites in alkaline solution by heating.

The reduction of alkali nitrite to nitric oxide and ammonia by an alkaline solution of dextrose containing an iron salt is now comprehensible in view of the formation of the complex iron salts which are produced with aldo- and keto-hexoses in alkaline solution. Oxanthrone behaves quite similarly to dextrose, and in both cases oxygen is unnecessary. C. S.

Nitrate and Nitrite Assimilation. XV. Iron and Oxygen as Necessary Agents for the Reduction of Alkali Nitrates.

OSKAR BAUDISCH (*Ber.*, 1919, 52, [B], 40—43. Compare preceding abstract).—Experiments are recorded which show that an alkali nitrate is quite unaffected by boiling in alkaline solution with ferrous carbonate or hydroxide in the absence of oxygen, but is reduced through the alkali nitrite to ammonia directly oxygen is admitted. Alkali nitrite is reduced to ammonia even in the absence of oxygen.

The author invokes his peroxide formula of alkali nitrates (A., 1916, i, 702) to explain the phenomenon. Probably the oxygen and the ferrous hydroxide form a compound, $\begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{Fe(OH)}_2$, and this and the alkali nitrate, reacting together like two peroxides, produce oxygen and alkali nitrite; the latter is then reduced to ammonia. C. S.

Influence of Salts on the Nitric-Nitrogen Accumulation in the Soil. J. E. GREAVES, E. G. CARTER, and H. C. GOLDTHORPE (*J. Agric. Res.*, 1919, 16, 107—135).—The object of the investigation was to determine the relative toxicity and stimulant action of various salts applied to a soil, as measured by the effect on the nitrifying organisms. The salts tested were the chlorides, nitrates, sulphates, and carbonates of sodium, potassium, calcium, magnesium, manganese, and iron. It was found that the toxicity of these salts was determined by the specific nature of the salt, and not by the ions. In order of decreasing toxicity, the salts were: sodium sulphate, sodium carbonate, calcium carbonate, potassium sulphate, potassium carbonate, ferric nitrate, sodium nitrate, magnesium sulphate, ferric sulphate, calcium nitrate, potassium nitrate, potassium chloride, magnesium nitrate, manganous carbonate, manganous chloride, manganous sulphate, ferric carbonate, magnesium chloride, sodium chloride, calcium chloride, calcium sulphate. Increase of toxicity with concentration was much more rapid in some cases than in others. The explanation of the toxicity is probably physiological, due to the action of the salt on the living protoplasm of the bacterial cell, the increased osmotic pressure of the soil solution being subsidiary.

Most of the salts acted as stimulants to nitrification in some at least of the concentrations used. Those which failed to give any stimulation were sodium sulphate and carbonate, calcium carbonate, potassium sulphate and carbonate, and ferric nitrate. Many of the nitrates caused large losses of nitric nitrogen, due to conversion into protein nitrogen, and not to denitrification. The fixation of nitrogen was specially stimulated by the nitrates of magnesium, iron, calcium, and manganese. [See *J. Soc. Chem. Ind.*, 1919, 297A.] J. H. J.

Preparation of Glycerol by Fermentation. KARL SCHWEIZER (*Helv. Chim. Acta*, 1919, 2, 167-172).—Glyceraldehyde and dihydroxyacetone are commonly regarded as intermediate compounds in the conversion of sugar into alcohol. It is possible, therefore, that they are also the precursors of the glycerol which is formed during alcoholic fermentation, in which case it might be possible to increase the yield of glycerol if the process is carried out in the presence of a reducing agent. Owing to the sensitive nature of the ferment, the problem resolves itself into finding a hardy species of yeast and a reducing agent which does not hinder its development. A technical pressed yeast, prepared with molasses, and sodium sulphite were found to answer the requirements. On the experimental scale, the best result was obtained in a Hayduck apparatus with a mixture containing 40 grams of sucrose, 2 grams of ammonium dihydrogen phosphate, 1 gram of dipotassium hydrogen phosphate, and 10 grams of pressed yeast in 400 c.c. of water, to which 30 grams of sodium sulphite were added when the fermentation had started. After twenty-four hours, fermentation had stopped, and as a mean of several experiments 21.3 grams of glycerol were obtained from 100 grams of sucrose. As might be expected, less glycerol was formed if the mixture was thoroughly aerated.

It is stated that some of the belligerent nations have applied sodium sulphite in the manufacture of glycerol by fermentation on the large scale during the war. J. C. W.

Fumaric Acid Fermentation of Sugar. FELIX EHRLICH (*Ber.*, 1919, 52, [B], 63-64).—The formation of free fumaric acid during the fermentation of sugar by *Aspergillus fumigatus* (Wehmer, this vol., i, 58) has been previously observed by the author during fermentation by *Rhizopus nigricans* (*Mucor stolonifer*) (A., 1912, ii, 192). C. S.

Determination of the Distribution of Nitrogen in Certain Seeds. J. F. BREWSTER and C. L. ALSBERG (*J. Biol. Chem.*, 1919, 37, 367-371).—Certain of the results have been reported previously (compare A., 1915, i, 760).—Yeast-nucleic acid, which was free from material giving a biuret reaction, was hydrolysed with 20% hydrochloric acid for twenty-five hours, and then analysed by the Van Slyke method for determining the distribution of

nitrogen in proteins. Fifteen % of the total nitrogen was found in the arginine fraction, although the nucleic acid contained no arginine. This indicates that in the determination of the distribution of nitrogen in materials containing nucleic acid by this method, erroneous results may be obtained, because purine and pyrimidine nitrogen may appear in the arginine fraction.

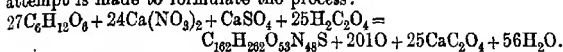
J. C. D.

The Influence of External Concentration on the Position of the Equilibrium Attained in the Intake of Salts by Plant Cells. WALTER STILES and FRANKLIN KIDD (*Proc. Roy. Soc.*, 1919, [B], 90, 448—470).—The authors have followed the course of intake of salts by carrot and potato tissue by measuring the changes in conductivity of the solution of a salt presented to the tissue, working with concentrations varying from $N/10$ to $N/5000$. Carrot tissue is much more suitable than potato tissue for work of this character, since the exosmosis from carrot into distilled water is slight, whilst that from potato is considerable. In the case of copper sulphate, exosmosis exceeds absorption at all concentrations, this being characteristic of toxic substances, and the initial rate of exosmosis increases with increase in concentration of the toxic solution. With aluminium sulphate, the curves showing the change in conductivity of the external solution were similar to those obtained with copper sulphate, although aluminium sulphate is not toxic. The authors suggest that this may be due to the absorption of the aluminium ion, its place being taken by hydrogen ions or some other ions, which results in an increase in the conductivity of the external solution.

Carrot tissue absorbs potassium, sodium, and calcium chlorides in all the concentrations examined, the absorption at first being approximately proportional to the external concentration. As the absorption progresses, however, it tends towards an equilibrium condition in which the ratio of internal to external concentration is not constant, but varies with the concentration. This ratio of final internal to final external concentration is called the absorption ratio, and may be expressed by the equation $y = kc^m$, where y is the final internal and c the final external concentration, k and m being constants. This is the adsorption equation, but the data given are regarded as inadequate to justify the conclusion that absorption of salts by the cell is an adsorption process. W. G.

Relationship between the Formation of Proteins and Acids in Leaves. ARTH. MEYER (*Ber. Deut. bot. Ges.*, 1918, 36, 508—513).—A review of the literature shows that slight protein formation accompanied by feeble deacidification and production of oxalate occurs in leaves kept in the dark; on exposure to light, the three processes occur to a greater extent. Protein and oxalate are readily formed in leaves exposed to light in an atmosphere free from carbon dioxide, and marked deacidification takes place simultaneously. The actions do not occur to more than a slight extent in the illuminated, colourless leaf.

The author is of the opinion that the carbohydrates react with nitrogen, sulphur, and phosphorus derived from inorganic salts to yield proteins; the bases of the salts are thereby liberated and neutralised by the organic acid produced in the leaves. An attempt is made to formulate the process:



Evidence in favour of such a scheme is deduced from the literature, and further quantitative data are promised.

H. W.

Utilisation of Dextrose and Lævulose by Higher Plants.

H. COLIN (*Compt. rend.*, 1919, 168, 697—699).—From an examination of etiolated leaves of beetroot, artichoke, and chicory fed by a root or a tubercle having a reserve of sucrose or inulin, the author produces further evidence in support of the view that lævulose is used by the cells more rapidly than is dextrose.

W. G.

Influence of certain Organic Compounds on the Development of Plants. III. G. CIAMICIAN and C. RAVENNA (*Atti It. Accad. Lincei*, 1919, [v], 28, i, 13—20. Compare A., 1918, i, 473).

—The effect of watering bean plants grown on cotton wool with 0·1% solutions of various compounds related fundamentally to the vegetable alkaloids has been studied; the bases tested were applied in the form of tartrates or phosphates. Of the three methylamines, methylamine is the least toxic and the slowest, and trimethylamine the most toxic and the most rapid, in its action; small, yellowish-brown spots appear on the veins and then on the whole surface of the leaves, which finally dry up. The action exerted by tetramethyl- and tetraethyl-ammonium salts is less poisonous than, and different in its manifestation from, that of the amines. Theobromine and dimethylxanthine exert effects moderate in comparison with those of caffeine and trimethylxanthine. Methyluric acid has a distinctly toxic action, slow in appearing. Piperidine exerts a slight effect, but allows the plants to attain complete maturity, whereas 1-methylpiperidine, dimethylpiperidylammonium tartrate, conine, acetyl-piperidine, and piperine are all more or less toxic. Unlike morphine, codeine and diacetylmorphine are markedly toxic. Cinchonine exhibits the same poisonous effects as quinine, but to a less degree. Atropine and cocaine are both toxic, the action of the latter being the more prompt and more intense. Papaverine and narcotine are somewhat more toxic than morphine and produce similar effects, and sparteine also has a poisonous action. Strychnine at first causes increased development of the plants, but these die later; nicotine also kills the plants, but in 0·01% solution is without effect. *iso*-Amylamine rapidly produces fatal effects. Aniline is less poisonous than acetanilide, and this less so than methylacetanilide.

The above results indicate that introduction of methyl groups increases the toxicity of a compound, confirmation of this rule

being obtained with catechol and guaiacol. Potassium salicylate causes only retardation in development, whereas methyl salicylate exhibits distinct, although belated, toxicity.

Experiments with carbamide, guanidine, cyanamide, and potassium cyanate and cyanide show that cyanamide is the most poisonous of the first three compounds, and is followed by guanidine; carbamide, on the other hand, produces extraordinarily rank development of the plants. The cyanate and cyanide, both poisonous, determine retarded growth.

Some of the above poisonous compounds exert an influence on the migration of the starch, treatment of the leaves with iodine solution demonstrating the persistence of the starch at places where the action of light is excluded. The formation of starch also is sometimes retarded, coloration of the leaves by iodine exhibiting discontinuity in the form of spots and veinings.

T. H. P.

Microchemistry of Plants. XII. Large Siliceous Bodies in the Leaf of *Arundo Donax*. XIII. Behaviour of Cystolites towards Salts of Silver and other Metals. HANS MOLISCH (*Ber. deut. Bot. Ges.*, 1918, **36**, 474—481. Compare this vol., i, 113).—Unusually large siliceous bodies, 72—108 μ long, 43—100 μ wide at the ends, and 11—54 μ wide at the middle, occur in the leaves of *Arundo Donax*; they are insoluble in all acids except hydrofluoric, and can readily be examined after treatment of the leaf with phenol.

All the cystolites which have been investigated possess the power of reducing silver nitrate or sulphate so strongly that they become blackened after a short period. This property can be conveniently utilised for the investigation of the distribution of cystolites in leaves, the effects being well marked even with small magnification. The deposition of silver is due to calcium carbonate, which encrusts the cystolites, and the action provides a confirmatory microchemical method for the detection of calcium carbonate in the plant. Cystolites become coloured red to bluish-violet in gold chloride solution, rust-red in ferrous sulphate, pale green in nickel sulphate, and lilac or pink in cobalt chloride or cobalt sulphate. The colorations are due to precipitates of the corresponding hydroxides caused by the calcium carbonate of the cystolites.

H. W.

Production of Alcohol from Algæ. E. KAYSER (*Ann. Chim. anal.*, 1919, [ii], **1**, 79—80).—See this vol., i, 193.

Carbohydrate Content of Lichens and the Influence of Chlorides on Alcoholic Fermentation. E. SALKOWSKI (*Zeitsch. physiol. Chem.*, 1919, **104**, 105—128).—Analyses of Iceland moss (*Lichen islandicus*) and reindeer moss (*Cladonia rangiferina*) are given. The former contains 59.45% of lichenin, 4.3% of fat, 4.73% of protein, 19.47% of organic matter, exclusive of lichenin, 2.01% of ash, and 10.04% of water. The latter contains 54.63% of lichenin, 2.59% of ether extract, 4.1% of protein, 26.96% of other organic sub-

stances, 10.59% of water, and 1.13% of ash. Hydrolysis of these two lichens with 2.5% hydrochloric acid or 6% sulphuric acid yields 60–66% of the dry weight of the raw material as dextrose. The sugar is fermentable. Sodium chloride disturbs the fermentation of dextrose according to the amount present. The concentration of dextrose also has an influence. A 12% solution of dextrose containing 4% of sodium chloride is completely fermented, and nearly so when 8% of the salt is present. Only 90% of the sugar is fermented when a 20% solution containing 4% of sodium chloride is tested. The equivalent quantity of calcium chloride exerts a more disturbing influence. The hydrolysates from the lichens contain not only the readily fermentable sugar, but also a substance which inhibits fermentation. It is possible this property belongs to the acids from the lichens. Lichens contain a readily hydrolysable cellulose. Lichenin is not converted into sugar by the diastatic ferments of the pancreas or saliva or plant diastases. Iceland moss contains at least 10.92% of lichen acids calculated as cetraric acid, $C_{30}H_{30}O_{12}$.
J. C. D.

Application of the Biochemical Method to the Study of Several Species of Indigenous Orchids. Discovery of a New Glucoside, Loroglossin. EM. BOURQUELOT and M. BRIDEL (*Compt. rend.*, 1919, **168**, 701–703).—Using the method previously described (A., 1906, ii, 386), the authors have proved the presence in the aerial organ of a number of species of orchids of one or more glucosides hydrolysable by emulsin. From one of these orchids, *Loroglossum hircinum*, Rech., a new glucoside, *loroglossin*, has been isolated, having m. p. 137° (corr.), $[\alpha]_D^{20} -42.97^\circ$. It is hydrolysed by warm dilute sulphuric acid, as well as by emulsin. In addition, the plants contain sucrose and a considerable amount of a dextrorotatory substance, which is not attacked by ferments.
W. G.

The Flavones of Rhus. C. E. SANDS and H. H. BARTLETT (*Amer. J. Bot.*, 1918, **5**, 112–119; from *Physiol. Abstr.*, 1919, **3**, 578).—The wood flavone of *Rhus typhina* and *R. glabra* is fisetin, which is regarded as an end-product of metabolism. The distinctive leaf flavone of *R. glabra* and *R. copallina* is myricetin, which is probably a plastic substance. The authors agree with Perkin's views (T., 1896, **69**, 1299–1303, 1303–1309; 1898, **73**, 1016–1019; 1900, **77**, 423–432) that the flavones of the wood and of the leaves of *Rhus* are different.
W. G.

Chemical Investigations of some Poisonous Plants in the Natural Order Solanaceæ. III. Occurrence of Noryscoyamine in Solandra longiflora. J. M. PETRI (*Proc. Linn. Soc. N.S.W.*, 1917, **41**, 815–822; from *Physiol. Abstr.*, 1919, **3**, 581).—The leaves of *Solandra longiflora* contain alkaloids to the extent of 0.17% of the dry weight, the chief one being solandrine, and hyoscyamine is also present.
W. G.

Toxic Constituents in the Bark of *Robinia pseudacacia*, L. BUHACHIRO TASAKI and USHIO TANAKA (*J. Coll. Agric. Tokyo*, 1918, **3**, 337—356).—A new toxic glucoside, *robitin*, was isolated from the bark of *Robinia pseudacacia*. The air-dried bark was extracted with water, and the filtrate heated for half an hour at 80—90°, after which it was refiltered. The second filtrate was concentrated at 40° under reduced pressure to one-tenth of its volume. Impurities were separated by lead acetate, the excess of lead was then removed, and the process of concentration repeated. A reddish-brown extract was obtained, which was poured into absolute alcohol, when a white, flocculent precipitate was produced; this was washed with alcohol and dried in a vacuum. The yield was 3% of the dried bark. As thus prepared, robitin is a pure white, odourless, somewhat bitter, hygroscopic, amorphous powder, easily soluble in water and acids, but insoluble in organic solvents. It contained 3% of ash. On hydrolysis, it yielded glucose and rhamnose. [See *J. Soc. Chem. Ind.*, 1919, 267A.] J. H. J.

Copper and Zinc as Antagonistic Agents to the "Alkali" Salts in Soil. C. B. LIPMAN and W. F. GERICKE (*Amer. J. Bot.*, 1918, **5**, 151—170; from *Physiol. Abstr.*, 1919, **3**, 586).—Pot cultures of barley were grown on soils containing sodium chloride, sulphate, and carbonate in toxic quantities, to which copper in the form of its sulphate, chloride, or carbonate, or zinc in the form of its chloride or sulphate, was added. It was found that the presence of copper or zinc brought about an increased yield. W. G.

Presence of Acetylmethylcarbinol in Saccharine Sorghum Silage. W. G. FRIEDEMANN and C. T. DOWELL (*J. Ind. Eng. Chem.*, 1919, **11**, 129—130).—Saccharine sorghum silage is found to contain a volatile compound which reduces Fehling's solution and is identified as acetylmethylcarbinol; the latter was previously shown to exist in cider vinegar. The fact that acetylmethylcarbinol yields acetic acid on oxidation renders untrustworthy the Duclaux method for estimating alcohols, since, according to this method, the proportion of ethyl alcohol is calculated on the basis of the amount of acetic acid formed on oxidation. The saccharine sorghum silage is the only one in which formic acid has been found, this observation being probably connected with the fact that acetylmethylcarbinol yields formic acid as one of its products of oxidation. In none of the other silages examined could the presence of volatile reducing compounds be detected. T. H. P.

General and Physical Chemistry.

Matter and Light. Attempt at the Synthesis of Chemical Dynamics. JEAN PERRIN (*Ann. Physique*, 1919, [ix], 11, 5—108).—A purely theoretical discussion in which the author endeavours to show that it is possible to develop a coherent theory, which sees in light the cause of chemical reactions, and which elucidates and correlates varied types of phenomena which at first sight seem quite different. According to the theory, dissociation or combination, phosphorescence, radioactivity, change of physical state, all obey one and the same fundamental law, which is connected with the internal structure of the atom. W. G.

Dispersion of Diamond. L. SILBERSTEIN (*Phil. Mag.*, 1919, [vi], 37, 396—406).—A mathematical paper in which the conception of electrical interaction of atoms is applied to the refractive properties of diamond, considered as a known assemblage of fixed atomic centres, each containing a single dispersive electron and becoming a doublet in the presence of an external electric field. J. F. S.

Regularities of the Second Kind in Line Spectra. J. E. PAULSON (*Zeitsch. wiss. Photochem.*, 1918, 18, 202—208).—The author, following the lead of Kayser, terms regularities between the wave-lengths of the various spectrum lines, regularities of the second kind. The present paper is a theoretical discussion of these regularities, in which it is shown that the magnetic resolution of the lines of a wave-length system does not follow such simple laws as that of the series lines. J. F. S.

Vacuum Arc Spectra of Various Elements in the Extreme Ultra-violet. J. C. MCLENNAN, D. S. AINSLIE, and D. S. FULLER (*Proc. Roy. Soc.*, 1919, [A], 95, 316—332. Compare this vol., ii, 125).—A vacuum arc spectrograph is described, together with the method of operation. The vacuum arc spectra of copper, aluminium, zinc, carbon, iron, tin, thallium, lead, nickel, cobalt, and cadmium have been measured down to $\lambda=1400$. The wave-lengths are compared in all cases with values obtained by other observers, and the intensities and frequencies are included in all the tables. In the case of zinc, the lines $\lambda\lambda=2025\cdot5(16)$, $1821\cdot8(3)$, $1589\cdot6(10)$, $1510\cdot4(1)$, $1491\cdot5(1)$, $1486\cdot2(6)$, $1478\cdot5(2)$, $1477\cdot6(4)$, $1457\cdot9(4)$, $1457\cdot5(4)$, $1451\cdot1(4)$, $1445\cdot0(3)$ were measured. The figures in brackets represent the intensities of the lines. For aluminium, the lines $\lambda\lambda=1989\cdot9(14)$, $1935\cdot1(4)$, $1930\cdot4(10)$, $1862\cdot8(32)$, $1854\cdot5(32)$, $1766\cdot6(4)$, $1761\cdot9(10)$, $1724\cdot3(10)$, $1720\cdot7(8)$, $1718\cdot5(4)$, $1670\cdot6(4)$, $1611\cdot8(14)$, and $1605\cdot6(12)$ were measured. In the case of copper, the lines $\lambda\lambda=2037\cdot3(6)$, $2026\cdot2(4)$, $2001\cdot0(4)$,

1979·6(4), 1748·6(4), 1739·7(4), 1721·8(6), 1708·5(4), 1704·9(2), 1693·4(4), 1692·5(1), 1686·7(4), 1684·6(2), 1681·7(1), 1679·1(2), 1674·6(2), 1671·5(2), 1670·1(2), 1651·9(2), 1642·1(8), 1594·2(8) were measured. The thallium arc was produced by placing metallic thallium in iron cups attached to iron poles; the lines measured in this case were $\lambda\lambda$ 1907·8(14), 1891·8(6), 1827·3(2), 1814·2(6), 1792·2(8), 1660·0(6), 1653·8(6), 1561·8(14), 1559·0(16), 1538·5(5), 1508·2(4), 1499·8(6), 1491·0(2), and 1478·0(4). With tin, the lines $\lambda\lambda$ 2152·5(12), 2041·2(2), 1941·0(1), 1899·8(20), 1831·4(6), 1811·2(20), 1756·6(16), 1741·3(1), 1699·5(10), 1489·2(6), 1475·2(15), 1438·3(4), 1437·3(4), 1402·4(4), and 1400·5(4) were observed. The lead arc was produced in the same way as that of thallium; the lines recorded in this case are 2170·5(8), 2060·5(8), 1925·8(2), 1913·7(4), 1904·2(2), 1898·7(2), 1895·5(2), 1821·7(14), 1796·5(10), 1744·2(1), 1741·1(2), 1726·2(10), 1682·5(12), 1671·6(12), 1597·6(3), 1555·8(12), 1511·7(4), 1494·7(1), 1492·7(1), 1434·0(5), and 1431·9. With a carbon arc, the lines $\lambda\lambda$ 2307·5(2), 2298·0(9), 2219·0(2), 2088·5(5), 1930·5(15), 1758·1(9), 1749·7(5), 1656·9(10), 1562·0(9), 1561·2(9), 1560·5(9), 1550·7(2), 1548·5(3), 1482·8(5), 1464·5(6) were recorded. A cobalt arc gave the lines $\lambda\lambda$ 2138·7(4), 2099·3(2), 2061·5(5), 2026·2(7), 1939·5(2), 1929·5(9), 1912·2(3), 1893·8(4), 1861·4(10), 1853·0(10), 1819·8(2), 1740·3(1), 1710·9(2), 1669·9(7). Mild steel electrodes were used for the production of the iron arc; the lines measured are $\lambda\lambda$ 2394·5(5), 2380·2(5), 2360·0(4), 2346·0(4), 2097·5(2), 2078·8(4), 2061·5(3), 1926·0(2), 1913·8(4), and 1894·3(3). In the case of nickel, forty-one lines lying between λ 2005·0 and λ 1650·1 were measured, but nothing of smaller wavelength than this. With the cadmium arc, the lines observed are $\lambda\lambda$ 1993·5(1), 1988·0(1), 1966·0(1), 1946·0(1), 1940·0(4), 1932·5(4), 1894·5(1), 1874·5(1), 1871·0(1), 1855·5(2), 1846·5(4), 1827·0(1), 1808·0(3), 1790·5(4), 1745·5(2), 1728·0(4), 1711·0(3), 1706·5(2), 1668·5(10), 1656·5(1), 1647·5(2), and 1526·5(1). Reproductions of photographs of the spectrograph and of all the spectra are appended to the paper.

J. F. S.

Ultra-violet Light Absorption of Unsaturated Compounds.

H. LEV (*Zeitsch. wiss. Photochem.*, 1918, **18**, 177—191).—The ultra-violet spectra of styrene, α -methylstyrene, β -methylstyrene, stilbene, methylstilbene, α -phenylstilbene, cinnamic acid, β -methylcinnamic acid, and α -phenylcinnamic acid have been investigated. In the case of styrene, a band is found at $1/\lambda = 4100$ ($c = 0\cdot001$, $d = 2$ mm.), and at ($c = 0\cdot01$, $d = 2\cdot5$ — $7\cdot0$ mm.) bands occur at $1/\lambda = 3440$ and 3550 . The introduction of a methyl group in the β -position displaces the original continuous absorption and the band 3440 toward longer wave-lengths, whilst the band 3550 vanishes. The introduction of a methyl group in the α -position brings about at higher concentrations a definite displacement toward the ultra-violet, and the absorption between 3400 and 3600 completely disappears. Stilbene possesses a deep band $1/\lambda = 3400$ ($c = 0\cdot001$ and $d = 1$ — 10 mm.); the introduction of a methyl group

into the ethylene group brings about a twofold change in the absorption spectrum: (i) a displacement of the continuous absorption towards the ultra-violet, and (ii) the bands are displaced in the same direction, or, in other words, at the position of maximum absorption the extinction coefficient is smaller. In the case of the derivatives of cinnamic acid, it is shown that β -methylcinnamic acid and α -methylstyrene are optically similar, whilst the same also applies to cinnamic acid and styrene.

J. F. S.

Absorption Spectra of Acid Hæmatin, Oxyhæmoglobin, and Carbon Monoxide Hæmoglobin. A New Hæmoglobinometer. H. S. NEWCOMER (*J. Biol. Chem.*, 1919, 37, 465-496).—Acid hæmatin has different spectral characteristics under varying conditions as to acid and solvent. The curve for material prepared in the manner described is constant and stable, for several days at least. The prominent band in the red has its deepest point at about 6620 Å.U. The other two bands in the visible spectrum are very shallow. There is a broad, general depression extending from 5100 to 5900 Å.U. which is divided by a very slight rise at 5480 Å.U. The great ultra-violet band of acid hæmatin is broader and shallower than in the case of oxyhæmoglobin, the broadening extending it further into the ultra-violet and obliterating the small peak at 3680 Å.U. which appears in the oxyhæmoglobin curve. There is beyond the peak at 3100 Å.U. a shallow but distinct band with its centre at 2780 Å.U. Beyond 2400 units, the absorption becomes very great. The further side of this band did not appear within the range of the instrument (2050 units). The β -band of oxyhæmoglobin is seen to be fainter than the α -band, but the difference in depth is slight. The great ultra-violet band is much deeper, the ratio of extinction coefficients being about eight. Oxyhæmoglobin has two further bands in the ultra-violet, at 3460 and 2760 Å.U., separated by a peak at 3100, somewhat higher than the corresponding one of acid hæmatin. The similarity in the ultra-violet of the absorption of the two substances would seem to indicate that it is due in large part to a radicle common to both. Carboxyhæmoglobin has an absorption similar to that of oxyhæmoglobin. In the visible, the bands are not so sharp and the transmission is not so great, particularly at the peak between the α - and β -bands. It is the lowness of this peak which accounts for the difference in shade between solutions of the two compounds. The visible bands of carboxyhæmoglobin are approximately of the same depth as the β -band of oxyhæmoglobin; they are shifted with respect to those of oxyhæmoglobin toward the violet; the great ultra-violet band is much deepened and shifted in the contrary direction. In the ultra-violet, the two peaks are higher than in the case of oxyhæmoglobin. The height of the peak at 3760 units and the depth of the band at 4190 units decrease very markedly with loss of CO from solution.

The amount of the extinction due to the admixed serum is only from one-fourth to one-seventh of the whole. The presence of

plasma can be neglected in discussing the visible absorption of these compounds. The blood in the superficial capillaries of the skin would be sufficient in quantity to absorb almost completely all the violet and ultra-violet light which might fall on it.

A "high transmission yellow" semaphore glass has an absorption curve which runs smoothly as a mean through the acid hæmatin curve.

The hæmoglobin value of this glass has been carefully estimated, and by this means a colorimetric method for the determination of hæmoglobin has been elaborated. A colorimeter of the Duboscq type is used.

J. C. D.

A New Sector Spectrometer. SAMUEL JUDD LEWIS (T., 1919, 115, 312—319).

Tyndallmeter for the Examination of Disperse Systems.

RICHARD C. TOLMAN and ELMER B. VLIET (*J. Amer. Chem. Soc.*, 1919, **41**, 297—300).—An instrument is described for measuring the strength of the Tyndall beam in suspensions, colloidal solutions, smoke, and mists. It consists of a 6—8 volt lamp, a condensing lens, and a diaphragm through which the beam of light enters the chamber containing the gas or solution. The strength of the beam is then determined by a Macbeth illuminometer which has been standardised with either a suspension of finely divided silica or an opaque glass.

J. F. S.

Relation between the Intensity of Tyndall Beam and Concentration of Suspensions and Smokes. R. C. TOLMAN, L. H. REYERSON, E. B. VLIET, R. H. GERKE, and A. P. BROOKS (*J. Amer. Chem. Soc.*, 1919, **41**, 300—303. Compare preceding abstract).—The strength of the Tyndall beam has been determined after passing through silica suspensions and ammonium chloride smokes of various concentrations. It is shown that, in general, for liquid suspensions and smokes there is a strict proportionality between the concentration and the strength of the beam, provided that the concentration does not become high enough to give an opacity which affects the results, and that the size of the particles remains the same throughout the series of measurements.

J. F. S.

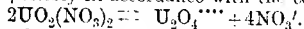
Disappearance of Smoke in a Confined Space. RICHARD C. TOLMAN, E. B. VLIET, W. MCG. PIERCE, and R. H. DOUGHERTY (*J. Amer. Chem. Soc.*, 1919, **41**, 304—312. Compare preceding abstracts).—The gradual disappearance of smokes in confined spaces has been investigated. It is shown that a smoke disappears in an enclosed space owing to coagulation, to settling, and to the diffusion of the particles to the walls, where they adhere. The rate of disappearance was determined by means of a Tyndallmeter in boxes 1 cu. m. capacity with smokes of burning acetanilide, benzoic acid, and resin. The rate of disappearance is markedly increased by

stirring the smoke, owing to the fact that it was brought in contact with the walls, where it adhered. The finer the state of subdivision of the smoke particles, the higher the readings on the Tyndallmeter owing to the greater reflecting surface of the particles. The rate of disappearance of a finely divided smoke of a given concentration is greater than that of a coarse smoke of the same concentration owing to the increased opportunity for coalescence. In smokes of the same size of particles, the rate of disappearance increases with the concentration owing to the increased chances of coagulation and removal by the walls. Since the increased concentration and increased subdivision both lead to a higher rate of disappearance, it is impossible to raise the optical density of a smoke beyond a certain point by the introduction of more smoke material.

J. F. S.

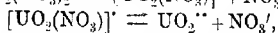
Rotatory Dispersive Power of Organic Compounds. IX. Simple Rotatory Dispersion in the Terpene Series. THOMAS MARTIN LOWRY and HAROLD HELLING ABRAM (T., 1919, 115, 300—311).

Principal Methods for the Determination of the Ionic Constitution of Solutions of Electrolytes and the Application of these to the Solution of Uranyl Nitrate. LEÓN GÓMEZ (*Anal. Fis. Quím.*, 1919, 17, 24—49).—A general discussion of the methods adopted to determine the mode of ionisation of an electrolyte in solution. With reference to the solution of uranyl nitrate, the results of the cryoscopic measurements of Dittrich (A., 1899, ii, 629) are examined. It is shown by extrapolation that the apparent molecular weight at infinite dilution is almost exactly one-third of the real molecular weight, so that an ionisation according to the scheme $\text{UO}_2(\text{NO}_3)_2 \rightleftharpoons \text{UO}_2^{++} + 2\text{NO}_3^-$ may be assumed. With increasing concentration, the ratio of the apparent to the real molecular weight approaches the value 2.5, so that even in concentrated solution the salt is ionised to a considerable extent, possibly in accordance with the equation



The values of the degree of dissociation, calculated on the assumption that the salt is a simple ternary electrolyte, are thus uncertain.

Dittrich's measurements of the equivalent conductivity show that up to an equivalent dilution of 4096 litres, the values of Λ do not converge to a limit. By forming the difference between each value of Λ and the next succeeding at double the dilution, it is shown that the difference decreases until the dilution $v=64$ litres is reached. From this point, the difference increases progressively throughout the range of dilution considered. This behaviour is attributed to the progressive ionisation of the salt, according to the equations $\text{UO}_2(\text{NO}_3)_2 \rightleftharpoons [\text{UO}_2(\text{NO}_3)]^+ + \text{NO}_3^-$ and



with subsequent hydrolysis at dilutions beyond $v=64$ litres.

The transport numbers for the anion were determined at concentrations between 0.0024 and 0.074 mol. per litre, the fall in concentration of UO_3 at the anode being measured. The curve obtained resembles that for a typical ternary electrolyte, and shows a minimum at concentration 0.015 mol. per litre, indicating a maximum concentration of $[\text{UO}_3(\text{NO}_3)]'$. At concentrations beyond 0.07 mol., the transport number approaches unity, the "metallic" radicle now forming part of the anion. At concentrations lower than 0.01 mol., the presence of UO_3'' is indicated.

The addition of ammonia to a uranyl solution precipitated the compound $(\text{NH}_4)_2\text{U}_2\text{O}_7$. This indicates the probable presence of the anion UO_3'' in the solution.

W. S. M.

Internally Complex Salts and Conjugated Salts of Alkali Metals. II. I. LIFSCHITZ and GEORG BECK (*Helv. Chim. Acta*, 1919, 2, 133—143. Compare A., 1914, ii, 512).—In the earlier communication, it was shown that the alkali salts of oximino-ketones and erythronitric acid have much lower electrical conductivities than the salts of simple acids in methyl-alcoholic or acetone solutions. It appeared at first sight that this abnormality was connected with the conjugated structure of the salts, which is superficially analogous to that of internally complex salts of the heavy metals. In the common cases of conjugated salts, no colour change accompanies electrolytic dissociation, and therefore it appeared to be of great interest to determine whether abnormal conductivity, in the above sense, is usual with such salts, as this would furnish a means of recognising conjugated structure. As far as solutions of the salts in methyl alcohol are concerned, it is found that conjugated structure causes no anomalies, which suggests that the peculiarities of the oximino-ketone salts require some other explanation.

The molecular conductivities of the sodium or potassium salts of the following compounds in methyl alcohol are recorded; hydriodic, acetic, propionic, butyric, valeric, benzoic, the three nitrobenzoic, benzenesulphonic, and *p*-phenolsulphonic acids, nitroethane, phenylnitroethane, *o*- and *p*-nitrophenylnitroethanes, the three nitrophenols, the five dinitrophenols, dinitroethane, phenyldinitromethane, nitroform, and phenyleyanonitromethane. These all show the same high conductivities, varying slightly with the nature of the cation, but free from abnormalities.

J. C. W.

Electrolytic Conductivity in Non-aqueous Solutions. III. Relations between the Conductivity of the Solute and several Physical Properties of the Solvent. HENRY JERMAIN MAUDE CREIGHTON (*J. Franklin Inst.*, 1919, 187, 313—318).—The results obtained in a previous paper (this vol., ii, 44) for the electrical conductivity of *p*-tolyltrimethylammonium iodide in thirteen organic solvents are used in considering the relationship between conductivity, viscosity, and association. The formula suggested

by Jones, $\Lambda v'/x = \text{constant}$, where $\Lambda v'$ is the equivalent conductivity of comparable equivalent solutions and η and x are the coefficient of viscosity and the association factor of the solvent respectively, is found to hold approximately at 25° for acetone, propaldehyde, propionitrile, nitromethane, epichlorohydrin, benzaldehyde, formic acid, and anisaldehyde, the mean value being 0.33 and the extremes 0.242 and 0.391. Methyl and ethyl alcohols, and especially acetic acid (0.054), give lower values, and benzonitrile and nitrobenzene higher values. The expression $\Lambda_{\infty}\eta$, which Jones also showed to be constant, has a mean value for these solvents, except formic and acetic acids, of 0.56 at 25°. A comparison of the percentage dissociation of *p*-tolyltrimethylammonium iodide in the same solvents, at three different dilutions, with the dielectric constants (ϵ) of the solvents shows the latter to be only one factor in deciding the former; the amount of polymerisation of the solvent appears also to be an important factor. This is shown in the figures for methyl alcohol ($\epsilon = 32.5-34.8$, $x = 3.43$) and nitrobenzene ($\epsilon = 33.4-37.4$, $x = 0.93$), in which the percentage dissociations at a dilution of $v = 128$ are 79 and 66 respectively. Similar variations are found in the figures for propionitrile, benzonitrile, and epichlorohydrin.

B. V. S.

Calculation of the Chemical Constants of Polyatomic Gases. AMÉLIE LANGEN (*Zeitsch. Elektrochem.*, 1919, 25, 25-45).

—A theoretical paper in which the chemical constants of oxygen, nitrogen, nitric oxide, carbon monoxide, carbon dioxide, water, and ammonia are calculated for the normal condition, and the following values obtained: nitric oxide, +0.92; oxygen, 1.021-0.539; carbon monoxide, -0.04; nitrogen, -0.05; carbon dioxide, -0.406; water, -1.930; and ammonia, -2.454. The oxygen value was obtained from four different equilibria. The results were used to calculate the Einstein function of the specific heat β_s , and the values, hydrogen 430, ammonia 67.5, water 30, carbon dioxide 7.23, oxygen 0.736, and nitric oxide 0.543 obtained. The order of the frequencies is what is to be expected from the physical properties of the substances, and can be confirmed, as far as the order of the value is concerned, from the moment of inertia of these gases.

J. F. S.

The Critical Temperature as a Single Function of the Surface Tension. MAURICE PRUD'HOMME (*J. Chim. Phys.*, 1918, 16, 405-410).—The surface tension, γ , is connected with the temperature by the two equations $\gamma = a - bt$ and $\gamma^{\frac{1}{2}} = a' - b't$ (compare A., 1916, ii, 600), which at the critical temperature become $a - bt = 0$ and $a' - b't = 0$. It is found that, for substances which obey the Eötvös-Ramsay law, $t_c = \frac{1}{2}(t_1 + t_2)$ or $t_c = \frac{1}{2}(a/b + a'/b')$. This also holds good for liquefied gases. Amongst substances which do not obey the Eötvös-Ramsay law, the organic acids conform fairly closely to the above equation, whilst the alcohols, phenols, etc., obey the simple relationship $\gamma = a - bt$.

W. G.

Vapour Pressure Regularities. II. W. HERZ (*Zeitsch. Elektrochem.*, 1919, **25**, 45—46. Compare *ibid.*, 1918, **24**, 333).—The author has calculated the value of the constant c of the Ramsay and Young vapour pressure formula $\theta_1/\theta_2 = T_1/T_2 + c(\theta_1 - T_1)$ for chlorine, bromine, iodine, oxygen, sulphur, nitrogen, phosphorus, arsenic, bismuth, argon, krypton, xenon, copper, silver, zinc, cadmium, mercury, tin, and lead, and finds that the value is not constant in a single case. In the case of the non-metals there is an approximation to a constant, but in the case of the metals the divergence is sometimes so great that the sign changes. These constants depend in a high degree on the boiling points, and it seems likely that the inconstancy may be due to inaccuracies in the determination of the boiling points. J. F. S.

Thermodynamics and Fractional Distillation. C. MARILLER (*Bull. Assoc. Chim. Sucr. Dist.*, 1918, **35**, 45—51).—Chenard's assertion that the vapours produced on distilling mixtures of alcohol and water tend to separate into layers of different density (A., 1914, ii, 623; 1916, ii, 175) is refuted on theoretical and experimental grounds. Using apparatus similar to Chenard's, and guarding against external cooling, the author found no evidence of stratification. J. H. L.

Formula giving the Density of a Fluid in the Saturated State. E. ARIÈS (*Compt. rend.*, 1919, **168**, 714—717).—The formula deduced is $v_1 - v_2 = \Gamma(y_1 - y_2)RT_c/8P_c$, where v_1 is the volume of the molecular mass of the fluid entirely in the state of vapour, and v_2 entirely in the liquid state, these thus giving the densities in the two states of saturation. The author has tested this formula in the case of carbon dioxide, stannic chloride, methyl formate, and heptane, and finds that his calculated results agree closely with those observed by Young. W. G.

Reasons for the Movements of Camphor [on Water] and Allied Phenomena. J. GEPPERT (*Physikal. Zeitsch.*, 1919, **20**, 78—83).—A number of experiments are described showing that many substances, such as phenacetin, acetanilide, chloral hydrate, sulphonal, menthol, thymol, atropine sulphate, phthalic acid, and quinine, exhibit the same violent movements as camphor does on the surface of clean water. The rate of movement of oily substances, such as oleic acid, is also considered. The reasons for the movement are attributed to solution of the solid and also of the vapour, and the back pressure thereby occasioned. J. F. S.

Adsorption Compounds. II. R. HALLER (*Kolloid Zeitsch.*, 1919, **24**, 56—66. Compare A., 1918, ii, 259).—A continuation of previous work on adsorption compounds; 0.5 gram of the dyes *m*-nitro-*p*-toluidine-red, *m*-nitroanisidine-red, *p*-nitro-*o*-anisidine-red, Sudan-G, Sudan-I, *p*-nitroaniline-red, alizarin-yellow G.G.W., fast-orange-O, brilliant orange, chromotrope 2R,

ponceau 2G, and *p*-nitrobenzeneazophtholsulphonic acid, dissolved in 50 c.c. of water, were treated with a 1% solution of brilliant-green as long as the latter was adsorbed. The adsorption products were isolated and characterised, and the colours produced when they were used to dye wool and cotton with tannic acid were noted.

J. F. S.

Laws of the Capillary Rise in Porous Paper. HANS SCHMIDT (*Kolloid. Zeitsch.*, 1919, **24**, 49--56).—A number of experiments are described, designed to ascertain the connexion between the rise of an acid solution in filter paper and the extent to which a drop of the liquid spreads itself when allowed to fall on to a sheet of the same paper. It is shown that the amount of spreading is the same whether the porous paper is horizontal or vertical in the case of dilute solutions of hydrochloric acid.

J. F. S.

Retardation by Sugars of Diffusion of Acids in Gels. JOHN ARTHUR WILSON (*J. Amer. Chem. Soc.*, 1919, **41**, 358--359).—A criticism of a paper by Graham and Graham (this vol., ii, 50). Compare Procter and Wilson (*T.*, 1916, **109**, 307) and J. A. and H. W. Wilson (*A.*, 1918, ii, 260).

J. F. S.

Osmosis and Swelling of Disperse Systems. WO. OSTWALD and K. MÜNDLER (*Kolloid. Zeitsch.*, 1919, **24**, 7--27).—A theoretical paper in which it is shown that the directly measured osmotic pressure of disperse systems is made up of two quantities: (i) the strict osmotic pressure, and (ii) an additional pressure, which is termed solvation, or swelling pressure. On the basis of this idea, a general solvation equation is established, $P_b = RTc_1 + kc_2^n$, in which P_b is the experimentally observed osmotic pressure, c_1 is the osmotic concentration, c_2 the swelling concentration, and k and n are constants. With dilute molecular or suspensoid dispersoids, the second factor of the equation disappears, and it passes over to the usual gas equation. On the other hand, in concentrated dispersoids, particularly in swelling gels, the osmotic concentration is very small, so that the first factor of the equation may be neglected. The expression $P_b = kc^n$ then, according to Posnjak and Freundlich, actually represents the dependence of the swelling pressure on the concentration in the case of gelatin and caoutchouc. The complete equation is applied to the osmotic measurements of solutions of sucrose, levulose, and lactose of Morse, and Berkeley and Hartley, over the range 0.1N--2.0N and 0--80°. The agreement between the values calculated by the formula and the experimental values is excellent. In the case of sugar solutions, $n=2$, so that as a first approximation the equation becomes $P_b = RTc_1 + kc_2^2$, but the value varies with the nature of the sugar and with the temperature. The osmotic pressure of very concentrated solutions of calcium ferrocyanide can be represented by the above equation to within 0.6%. In the case of con-

centrated sugar and calcium ferrocyanide solutions, the share of the total pressure due to the swelling pressure is very large. It increases, for example, with sucrose, with the concentration from 5% to 63% of the total pressure, and in the case of calcium ferrocyanide to 71%. It is also shown that the osmotic pressure of the hydrosols of iron, thorium hydroxide, and copper ferrocyanide follows the reduced solvation formula and also the swelling formula of Posnjak and Freundlich, a confirmation of the view that the taking up of water by such dispersoids is to be regarded more as the swelling of a liquid colloid than a simple osmotic process. The solvation formula does not hold for those systems in which internal changes in the state of aggregation occur with changes in concentration. The value of n lies always between 1.5 and 4.0, but most often it is found between 2 and 3. J. F. S.

Theory of Solubility. ALBERT COLSON (*Compt. rend.*, 1919, 168, 681—684. Compare A., 1916, ii, 475).—A theoretical discussion of certain points arising out of his formula

$$425L = T(V + \epsilon)idC/dT,$$

expressing all the particularities of solubility, where L is the heat of saturation, ϵ is the contraction of the final system, V is the volume of the solvent which saturates the dissolved molecule, C is the concentration or weight of anhydrous salt in 100 grams of a solution saturated at T° . W. G.

Electrical Synthesis of Colloids. THE. SVEDBERG (*Kolloid. Zeitsch.*, 1919, 24, 1—7).—Three processes are described by which highly disperse metal colloids may be produced. The author prefers to call these processes electrothermal colloid syntheses. A thin sheet of gold or silver is attached by gum arabic to a plate of glass which is immersed in ethyl alcohol. Two iron wires, attached to a 440-volt circuit and arranged to carry 10 amperes, are inserted in the liquid and brought into contact with the metal foil. Immediately, the metal round the iron poles is vaporised, and on condensation in the alcohol produces alco-sols. In the second process, narrow strips of gold, silver, zinc, and tin foil are attached to glass plates in the above-mentioned manner. The ends of the strips are thickened by a somewhat thicker piece of copper. Two iron wires, as before, are brought into contact with the copper, when the strip of foil between is entirely converted into the sol. In the third method, thin wires or strips of platinum, copper, lead, zinc, and aluminium are fastened to two thick iron wires immersed in alcohol, and a current passed, when the sols of these metals are produced. The process consists in the melting of the metal, which forms a number of small globules by capillary forces, and between which a number of small arcs are set up. This vaporises the metal, which condenses in the cooler regions to form highly disperse sols. The production of the sol depends more on the current strength than on the voltage employed. J. F. S.

Colours of Colloids. II. WILDER D. BANCROFT (*J. Physical Chem.*, 1919, **23**, 1—35. Compare A., 1918, ii, 102).—A continuation of the discussion commenced in a previous paper (*loc. cit.*). The various colour effects produced by reflection and refraction of light are particularly considered in this communication.

J. F. S.

Colloid Chemistry of Indicators. II. WOLFGANG OSTWALD (*Kolloid. Zeitsch.*, 1919, **24**, 67—69. Compare A., 1912, ii, 439).—In a previous paper the author advanced the view that the colour change of indicators in many cases is a colloidal or disperse chemical process. The present paper is a résumé of the results of experiments on congo-rubin, which tend to substantiate the author's view. In aqueous solution, congo-rubin (sodium salt of benzidinebisazo- β -naphtholsulphonaphthionic acid) is a highly disperse system, intermediate between that of a typical colloid and a molecular disperse system. It is negatively charged and has a red colour, which is changed to blue by the addition of acids. This change is also brought about by the addition of a large number (seventy-five) of neutral salts, by alkaline salts, such as sodium carbonate, and by bases like barium hydroxide. On dilution, the blue solutions again become red; elevation of temperature, or the addition of alcohol, acetone, or pyridine, brings about the same reversal of colour change. By a further addition of an electrolyte to the blue solution, a precipitation of the colour substance is effected. The precipitate, on washing with water, passes into solution as a blue to violet hydrosol. It is stated that the blue solutions are less highly disperse than the red solutions, and on keeping a solution which has just turned blue, a slight precipitation occurs, which leaves a red solution. This solution may be turned blue by further addition of electrolyte. The red solutions contain a still more highly disperse orange-coloured fraction.

J. F. S.

Oscillation Method for Measuring the Size of Ultra-microscopic Particles. P. V. WELLS and R. H. GERKE (*J. Amer. Chem. Soc.*, 1919, **41**, 312—329).—The diameter of the particles of gaseous dispersoids (in smoke) has been determined by an oscillation method. A quantity of the smoke is brought into the field of an ultramicroscope which lies in a rapidly alternating electrostatic field, and the path of the particles photographed. In this way the actual oscillations are obtained, and a measurement of the amplitude gives the distance travelled by the particle between two reversals of the current. Then, by Stokes's law, the motion of a particle in an electrostatic field is given by $Xe = 3\pi\eta dv$, where X is the field in volts per cm., e the electronic charge (that is, 1.59×10^{-20}), d the diameter in cm., η the viscosity of the medium, and v the velocity. It is shown that the diameter varies from 5×10^{-6} to 10^{-4} , and that the particles rapidly coalesce.

J. F. S.

Chemical Resistance. II. Applications of the Theory of Quanta to Chemical Dynamics. SHINKICHI HORIBA (*Mem. Coll. Sci. Kyoto Imp. Univ.*, 1918, **3**, 223—234. Compare A., 1916, ii, 305).—A mathematical paper in which, by an application of the theory of quanta, and on the hypothesis: "The reacting substances can only react when they are present in a certain elemental sphere of a reaction in a stoicheimetical relation by their own kinetic energy, but the reaction will begin only when they are transformed into an active form by absorbing some energy from the surrounding medium," calculations of chemical resistance have been carried out. On this hypothesis of the mechanism of a chemical reaction, chemical resistance can easily be separated into two terms: (1) a term inversely proportional to the probability that the molecules of the reacting substances encounter in a stoicheimetical relation in an elemental sphere by their own kinetic energy, and (2) a term proportional to the probability of the energy transport to reacting molecules from their surrounding medium.
J. F. S.

Crystal Gratings and Bohr's Atom Model. M. BORN and A. LANDÉ (*Ber. deut. physikal. Ges.*, 1918, **20**, 202—209).—A mathematical paper in which the radius and number of electrons situated in the various rings of the metals of the alkalis and of the halogens are calculated. The elastic compressibility of the alkali haloids is calculated, and values obtained are about twice as large as the experimentally determined values. The absolute dimensions of the grating constant, δ , have been calculated, and the values indicate that the substances are twice as soft as the theory demands.
J. F. S.

Calculation of the Compressibility of Regular Crystals from the Theory of the Grating. M. BORN and A. LANDÉ (*Ber. deut. physikal. Ges.*, 1918, **20**, 210—216. Compare preceding abstract).—The compressibility of the chloride, bromide, and iodide of sodium, potassium, and thallium has been calculated by means of the formula $\kappa = 4.26 \times 10^{-14} (\mu_{+} + \mu_{-}) / \rho^2$ on the basis that $n=9$ and not 5, as was taken to be the case in the previous paper. The value of n has been calculated from the observed compressibilities, and a mean value 8.76 obtained. Using the value 9, a good agreement is found between the calculated and experimental values. In the case of calcium fluoride, to which the calculations were extended, $\kappa = 1.10 \times 10^{-12}$, whilst the experimental value is 1.16×10^{-12} .
J. F. S.

The Cubic Atom Model. M. BORN (*Ber. deut. physikal. Ges.*, 1918, **20**, 230—239).—The author, from a survey of the properties of the halogen derivatives of the alkalis, considers the cubic atom model is well founded, and whilst holding to the principles set down by Bohr, considers the matter mathematically with the object of bringing certain abnormalities into line with the general

theory. The question of the tetrahedral carbon atom is also considered.

J. F. S.

Calculations of Ionic Charges in Crystals. J. WIMMER (*Physikal. Zeitsch.*, 1919, 20, 92—93).—A theoretical paper in which it is shown that the ionic charges of diatomic crystals or crystals which can be regarded as made up of two equivalent atomic groups, and for which the grating structure is known, can be calculated by means of the formula $v/z = (G_1 + G_2) / \sqrt{G_1 G_2}$, in which v represents the valency, z the number of electrons, and G_1 and G_2 the atomic or molecular weights of the atoms or groups composing the molecule. The charges have been calculated for the crystals potassium chloride, sodium chloride, calcium fluoride, silica, calcium carbonate, potassium bromide, potassium iodide, sodium fluoride, lithium fluoride, and zinc sulphide. In the case of the first-named five substances, the value of the Drude constant k has been calculated.

J. F. S.

The Theory of Duplex Affinity. SAMUEL HENRY CLIFFORD BRIGGS (T., 1919, 115, 278—291).

Laboratory Apparatus for Rapid Evaporation. E. C. MERRILL and CLARE OLIN EWING (*J. Ind. Eng. Chem.*, 1919, 11, 230).—Rapid evaporation of liquids is effected by passing a blast of heated air across the basins on the steam-bath. The air is forced through a brass cylinder containing cotton wool to act as a filter, and then through a copper coil, which is heated in the bath, and the outlet of which is connected with a series of blowers. Each of these is provided with a glass tap, and its height above the basin can be adjusted as desired. [See, further, *J. Soc. Chem. Ind.*, 1919, 268A.]

C. A. M.

Theobald van Hogelande. F. M. JAEGER (*Chem. Weekblad*, 1919, 16, 179—180).—The work "Merces Alchimistarum," Frankfurt-am-Mayn, 1610, attributed to Theobald van Hogelande (A., 1918, ii, 437), is shown to be a reprint of a German translation of his "De Alchimie Difficultatibus," Frankfurt, 1600.

W. S. M.

Inorganic Chemistry.

An Unusual Sulphur Crystal. F. RUSSELL BICHOWSKY (*J. Washington Acad. Sci.*, 1919, 9, 126—131).—A crystallographic description is given of a well-developed crystal, D 2·01, of sulphur which was obtained accidentally by adding a hot alcoholic solution of ammonium polysulphide to a mixture of benzonitrile, hydroxylamine hydrochloride, and ether.

L. J. S.

The Behaviour of Sulphur towards Carbonaceous Matter at High Temperatures. J. P. WIBAUT (*Rec. trav. chim.*, 1919, **38**, 159—162).—When sugar, or the carbon obtained by charring it, or wood charcoal, is mixed with sulphur and the mixture heated in a closed crucible to a bright red incandescence, in each case a product is obtained which, after extraction first with carbon disulphide and then with ether, is found to contain sulphur to the extent of from 3—6%. Whether this sulphur is chemically combined or only absorbed is not decided. W. G.

Tellurium Sulphide. AARON M. HAGEMAN (*J. Amer. Chem. Soc.*, 1919, **41**, 329—341).—The introduction of hydrogen sulphide into an aqueous solution of tellurous acid at ordinary temperatures or below causes the immediate production of a reddish-brown precipitate, which is represented by the formula TeS_2 . The production of this compound is independent of the acid concentration. At temperatures below -20° , tellurium sulphide is a stable compound, but at temperatures above -20° , dissociation takes place. At temperatures near -20° this dissociation is slow, whilst at higher temperatures dissociation takes place more rapidly. The degree of dissociation at any time or temperature may be determined by the amount of sulphur which can be extracted by carbon disulphide. Dissociation never continues to completion. The dissociated mass extracted with carbon disulphide always retains at least 0.95% sulphur. This sulphur does not exist as a sulphide of tellurium which is decomposed by hydrochloric or hydrobromic acid of any strength, nor does it exist as a variety of sulphur insoluble in carbon disulphide. The compound TeS , often described, has no existence. The production of TeS_2 is independent of the medium in which the reaction is effected, for the action of hydrogen sulphide on solutions of tellurium tetrachloride in a large number of organic solvents gave exactly the same product. The dissociation and stability of tellurium sulphide is solely a question of temperature. Tellurium tetrachloride is found to be soluble in benzene, toluene, methyl alcohol, ethyl alcohol, *n*-butyl alcohol, amyl alcohol, benzyl alcohol, xylene, chloroform, and ethyl acetate, sparingly so in light petroleum, benzaldehyde, acetone, isopropyl bromide, and carbon tetrachloride, and insoluble in carbon disulphide. J. F. S.

Formation of Ammonia at High Temperatures. E. BRINER (*Helv. Chim. Acta*, 1919, **2**, 162—166. Compare this vol., ii, 148).—A discussion of Maxted's recent work (*T.*, 1918, **113**, 168, 386). In the first place, it is shown that the T^2 terms in Maxted's two formulae have merely a corrective influence, and consequently they cannot be very significant in regions of temperature in which they have not been tested experimentally. This explains the great divergences between the values of K obtained from the two formulae; at 1000° abs. up to which point both formulae have been tested by experiment, there is agreement; at 2000° , the first

formula gives a value for K which is three times that derived from the second; at 3000° , the ratio is 10 to 1, and at 4000° , 100 to 1. Furthermore, assuming that at high temperatures the reaction is of the same nature as at lower temperatures, namely, one between molecules of nitrogen and hydrogen, these gases should unite completely at about 6000° , according to the first formula, and, in general, a gaseous mixture should become more and more complex with rise of temperature. This is contrary to the conclusions obtained by spectroscopic investigations, which clearly prove the elementary nature of the substances present in the hottest stars.

Such difficulties disappear if account is taken of the dissociation of the molecules into atoms (compare A., 1916, ii, 215). According to recent investigations, gases like hydrogen contain appreciable proportions of free atoms at much lower temperatures than was at one time supposed. The extra production of ammonia at high temperatures may be explained, therefore, by the greater kinetic energy of the free atoms of nitrogen and hydrogen. J. C. W.

Potassium Ammonosodiate, Potassium Ammonolithiate, Rubidium Ammonosodiate, and Ammonolithiate. EDWARD C. FRANKLIN (*J. Physical Chem.*, 1919, **23**, 36—53).—A number

of reactions between metallic amides in ammonia solution have been carried out, and as a result several ammono-salts have been isolated and characterised. These salts stand in the same relationship to ammonia as do the zincates, aluminates, and plumbites to water. A very complete list of the ammono-salts hitherto prepared is given. *Dipotassium ammonosodiate*, $\text{NaNK}_2 \cdot 2\text{NH}_3$ or $\text{NaNH}_2 \cdot 2\text{KNH}_2$ or $(\text{Na}[\text{NH}_2]_3)\text{K}_2$, is prepared (i) by the action of potassamide on sodamide in liquid ammonia solution, (ii) by the action of sodium iodide on an excess of potassamide in liquid ammonia, and (iii) by the action of sodium on potassamide in liquid ammonia in the presence of a small quantity of platinum black. This compound crystallises well, and does not lose ammonia at 100° in a vacuum; at higher temperatures it melts, loses ammonia, and attacks the containing glass vessel. *Mono-rubidium ammonosodiate*, $\text{NaNHRb} \cdot \text{NH}_3$ or $\text{NaNH}_2 \cdot \text{RbNH}_2$ or $(\text{Na}[\text{NH}_2]_2)\text{Rb}$, is formed by the action of sodium and rubidium simultaneously on liquid ammonia. This compound is readily soluble in liquid ammonia, and is violently decomposed by water with the formation of the hydroxides of the metals. *Dirubidium ammonosodiate*, $\text{NaNRb}_2 \cdot 2\text{NH}_3$ or $\text{NaNH}_2 \cdot 2\text{RbNH}_2$ or $(\text{Na}[\text{NH}_2]_3)\text{Rb}_2$,

is formed from the mother liquors of the previous compound by the addition of a large excess of rubidamide. This compound is considerably more soluble than the preceding compound in liquid ammonia. *Dipotassium ammonolithiate*, $\text{LiNK}_2 \cdot 2\text{NH}_3$ or $\text{LiNH}_2 \cdot 2\text{KNH}_2$ or $(\text{Li}[\text{NH}_2]_3)\text{K}_2$, is prepared by the action of potassamide on lithium iodide in liquid ammonia solution, and also by the action of lithium and potassium simultaneously on liquid

ammonia in the presence of platinum black. The salt forms minute, colourless crystals, which are practically insoluble in liquid ammonia. It is decomposed by acid amides and ammonium salts of oxygen and halogen acids (that is, by ammono-acids), with the formation of the corresponding salts of lithium, potassium, and ammonium. *Monorubidium ammonolithiate*, LiNHRb.NH_3 or $\text{LiNH}_2.\text{RbNH}_2$ or $(\text{Li}[\text{NH}_2]_2)\text{Rb}$, is prepared by the action of an excess of a solution of rubidamide in ammonia on metallic lithium in the presence of platinum black. A white, crystalline compound is obtained, which is sparingly soluble in liquid ammonia. It is decomposed by ammono-acids and by water, as in the preceding case. Attempts were made to separate rubidamide from potassium by crystallisation from liquid ammonia, but without success, for these two substances form isomorphous mixtures which are relatively richer in rubidamide than the solution from which they separate.

J. F. S.

Thermal Decomposition of certain Inorganic Trinitrides.

E. MOLES (*J. Chim. Phys.*, 1918, **16**, 401—404. Compare *ibid.*, 1917, **15**, 51).—A claim for priority over Hitch (compare A., 1918, ii, 398).

W. G.

Method of Treating Beryl for the Extraction of Glucinum.

H. COPAUX (*Compt. rend.*, 1919, **168**, 610—612).—One part of powdered beryl is heated with two parts of sodium silicofluoride at 850° for thirty to forty minutes. At this temperature, the sodium silicofluoride decomposes, giving silicon fluoride, which attacks the beryl, giving glucinum fluoride and aluminium fluoride, which in turn combine with the sodium fluoride to give the corresponding double fluorides. The material is extracted with boiling water, in which the sodium glucinum fluoride dissolves, and the extract, after filtration, contains practically the whole of the glucinum in this form along with a little alumina and silica. A slight excess of boiling sodium hydroxide solution is added to the filtrate, and the precipitated oxides are collected and redissolved in sulphuric acid. The solution is concentrated, and the glucinum sulphate is allowed to crystallise out. By this method, 90% of the glucinum present in the mineral may be readily recovered.

On this process is based a method for the estimation of glucinum in beryl, using four parts of sodium silicofluoride to one part of beryl. The precipitation with sodium hydroxide is omitted, and an aliquot portion of the filtered aqueous extract is evaporated with an excess of sulphuric acid in a platinum dish until white fumes appear. The residue is dissolved in water, and an excess of ammonium hydroxide is added. The precipitate is filtered off, washed, dried, ignited, and weighed. Any silica in it is removed by means of hydrofluoric acid, and the aluminium and glucinum oxides are separated by Wunder and Weger's method (compare A., 1912, ii, 687).

W. G.

Reaction between Sodium Chloride Solution and Metallic Magnesium. WILLIAM HUGHES (T., 1919, 115, 272—277).

The Hammer-hardening of Lead, Tin and Thallium. PAUL NICOLARDOT (*Compt. rend.*, 1919, 168, 558—560).—Lead, thallium, and tin all undergo hammer-hardening, but they anneal spontaneously at the ordinary temperature, the rate of annealing rising with rise in temperature. W. G.

The Extraction of Thallium from Pyrites Flue Dust. GEORGE SISSON and J. S. EDMONDSON (*J. Soc. Chem. Ind.*, 1919, 38, 70r).—The dust collected from the flues situated between the pyrites kilns and the Glover tower of a sulphuric acid plant was found to contain 0.25% of thallium, representing about one part of thallium per million of pyrites burnt. The thallium was isolated by extracting the dust with dilute sulphuric acid and precipitating with hydrochloric acid. The crude thallium chloride was purified, dried, and reduced to metal by fusion with potassium cyanide and sodium carbonate, or, alternatively, with zinc. E. H. R.

Chemistry of Aluminium and Aluminium Alloys. JOHN G. A. RHODIN (*Trans. Faraday Soc.*, 1919, 14, 134—149).—Experiments dealing with the working up of scrap aluminium are described. The specific gravity of aluminium containing various quantities of an equal mixture of copper and zinc has been determined, and it is shown that the density curve rises rapidly, but with decreasing rate, to 90% aluminium; between 90% and 80% aluminium, the curve is a slowly rising straight line which has an inflexion point somewhere about 76%. Aluminium is stated to dissolve alumina, and a method is devised for the estimation of the metallic aluminium apart from the alumina. A quantity of an aluminium alloy (2 grams) is placed in a tall beaker with 60 c.c. of 10% sodium hydroxide solution and heated on a sand-bath until the reaction becomes violent, after an induction period, when it is removed and cooled. The reaction is then completed by further heating on the sand-bath. The black residue is collected and dissolved in nitric acid (D 1.2). The two solutions thus obtained are analysed according to well-known methods. Comparison of the analytical results with the composition deduced from the specific gravity of the alloy showed a remarkably good agreement. By heating pure aluminium powder in air until the increase in weight corresponds with the formation of a compound Al_2O_3 , a light grey, non-metallic powder is obtained. Boiling this powder with 10% sodium hydroxide dissolves a portion of it and leaves insoluble a light grey oxide, Al_2O_3 . A number of determinations of the specific heat of aluminium alloys of copper and zinc are given. The following values were obtained: 98.6% aluminium, 0.2081; 90% aluminium, 10% copper, and 10% zinc, 0.1918; 80% aluminium, 20% zinc, 0.1844.

In the discussion on the paper, CLAUDE T. J. VAUTIN stated

that he had isolated the oxide Al_2O_3 , a compound which produced a brilliant light under air oxidation. J. F. S.

The Formation of Troostite at Low Temperature in Carbon Steels and the Influence of the Temperature of Emersion in Interrupted Tempering. A. PORTEVIN and GARVIN (*Compt. rend.*, 1919, 168, 731—733).—With velocities of tempering considerably higher than the critical velocities, by interrupting the tempering, very marked reheating may be observed, at temperatures down to 450° , and troostite is formed. The troostite is formed directly and immediately from the solid solution γ -iron-carbon at temperatures much lower than those at which it is formed by continuous tempering. With a velocity of tempering near to that of the critical velocity, it was possible to observe the formation of troostite at even lower temperatures (380°). If the velocity is inferior to the critical velocity, the reheating being produced at high temperatures during the period of rapid cooling, troostite is always obtained, and the temperature of emersion does not appreciably affect the structure and the hardness. With rapid tempering, it is possible, without appreciably altering the hardness, to stop the tempering at temperatures in the neighbourhood of 350° . W. G.

Structure of Iron-Carbon-Chromium Alloys. TAKEJIRŌ MURAKAMI (*Sci. Rep. Tohoku Imp. Univ.*, 1918, 7, 217—276).—An investigation of the structure of 115 chromium-iron, chromium-carbon, and iron-carbon-chromium alloys. The influence of chromium on the magnetic critical point from A_2 was investigated, and it was found that it decreases at first slowly and then rapidly as the chromium content increases.

In the annealed alloys, the chromium carbide present is Cr_4C . At high temperatures, this decomposes into Cr_3C_2 and chromium. Three double carbides of iron and chromium were detected, namely, $\text{Fe}_3\text{C}_2\text{Cr}_4\text{C}$, $(\text{Fe}_3\text{C})_9\text{Cr}_4\text{C}$, and $(\text{Fe}_3\text{C})_{18}\text{Cr}_4\text{C}$. A portion of a thermal equilibrium diagram for the ternary system was drawn up. The binary system iron-chromium is a continuous series of solid solutions with a minimum about 70% of chromium. In the solid state, a certain undetermined solubility of the carbide Cr_4C in chromium occurs. Cr_7C_3 and the double carbide $(\text{Fe}_3\text{C})_9\text{Cr}_4\text{C}$ form an uninterrupted series of solid solutions. The eutectic in the Cr_4C -Cr series occurs at about 1.8%. [See, further, *J. Soc. Chem. Ind.*, 1919, 257A.] F. C. TH.

The Reduction of Tungstic Oxide. C. W. DAVIS (*J. Ind. Eng. Chem.*, 1919, 11, 201—204).—To obtain a satisfactory reduction of tungstic oxide to metallic tungsten, the material must be freed from water, which is best effected by a current of air at about 500° . On reducing the dried oxide with carbon, a blue or purple oxide is produced at 650° to 850° , a chocolate-brown mixture of oxides at 900° to 1050° , and metallic tungsten above 1050° .

The proportion of carbon required for the reduction ranges from 1:10 to 1.6:10, according to the temperature, time, and other conditions. Excess of carbon can be removed to a considerable extent by washing the product with water. When hydrogen is used as the reducing agent, the mixture of brown oxides is formed at 800° to 900°, whilst at 1080° a pure tungsten deposit (for example, 99.4%) is obtained. Reduction with gasoline vapour yields a product containing about 98% of tungsten with a considerable amount of carbon. [See, further, *J. Soc. Chem. Ind.*, 1919, 260A.] C. A. M.

The Partial Purification of Zirconium Oxide. A. J. PHILLIPS (*J. Amer. Ceram. Soc.*, 1918, 1, 791—800).—Zirconia may be freed from iron oxide by mixing it with 4% of finely ground petroleum coke, making the mixture into balls, and heating them at 900° in a vertical cylindrical furnace (heated externally) through which a current of moist chlorine is passed. The reversible reaction $\text{FeCl}_3 \rightleftharpoons \text{FeCl}_2 + \text{Cl}$ constantly tends to form an equilibrium, which leaves some of the iron in the zirconia. If the rate of passage of the chlorine is increased beyond the requisite chlorine tension, chlorine is absorbed until the tension is reduced. With insufficient chlorine, the ferrous chloride is reduced. The water vapour present serves to produce hydrogen chloride, in which the ferrous chloride is readily volatile, whilst the zirconia is not affected. Hydrogen chloride without any free chlorine does not reduce the iron oxide below 0.5%. If the zirconia is heated by passing hot gases through it, the action of the chlorine is irregular and inefficient. Various methods of purification by fusing the zirconia with various salts proved unsatisfactory as far as the removal of the iron was concerned. [See *J. Soc. Chem. Ind.*, 1919, 252A.] A. B. S.

Mineralogical Chemistry.

Pyromorphite Group. M. AMADORI (*Gazzetta*, 1919, 49, i, 38—102).—A summary and discussion of previous papers (A., 1913, ii, 216; 1915, ii, 358; 1918, ii, 365). T. H. P.

Non-identity of the Copper Silicates, Plancheite and Shattuckite. WALDEMAR T. SCHALLER (*J. Washington Acad. Sci.*, 1919, 9, 131—134).—A reply to F. Zambonini (A., 1918, ii, 170). Although his new analysis of plancheite from the French Congo leads to nearly the same formula, $6\text{CuO} \cdot 5\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, as that for shattuckite ($2\text{CuO} \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$) from Arizona, the difference in the refractive indices is sufficient to prove that the two minerals are distinct. The highest value for plancheite ($\alpha=1.645$, $\gamma=1.715$) is less than the lowest value for shattuckite ($\alpha=1.752$, $\gamma=1.815$). L. J. S.

Analytical Chemistry.

A New Indicator for Bases and Acids. MARC CHAUVIERRE (*Bull. Soc. chim.*, 1919, [iv], **25**, 118—119).—The reagent is prepared by boiling red beetroot with water and filtering the extract. It is a violet-red, opalescent solution, which is turned deep yellow with alkalis and retains its colour with acids. It is sensitive to both weak and strong inorganic and organic acids. Its colour is restored by sulphuric acid diluted to 1 in 10,000. Test papers cannot be prepared from it, as it does not fix on paper. W. G.

End-point in Oxidation Titrations determined by means of the Potentiometer. I. M. KOLTHOFF (*Chem. Weekblad*, 1919, **16**, 408—416).—When a reducing agent is titrated by means of an oxidising agent, the potential difference between the solution and an irreversible electrode immersed in it, measured against a normal electrode, varies in value during the titration, and in the neighbourhood of the end-point undergoes a rapid change. Expressions are deduced for the *E.M.F.* at the end-point and for the equilibrium constant of the reaction in terms of the normal potentials of the oxidising and the reducing agents. With the help of these, the sharpness of the end-point is discussed in relation to the magnitude of the equilibrium constant. W. S. M.

Arsenious Oxide as a Standard Substance in Iodometry. ROBERT M. CHAPIN (*J. Amer. Chem. Soc.*, 1919, **41**, 351—358).—Using weight burettes, solutions of highly purified arsenious oxide have been tested as to their trustworthiness as standards in place of iodine solutions. In six titrations of pure arsenious oxide against pure iodine, very precise results were obtained, the average of which agreed to within 1 in 3600 of the theoretical value. It is shown that arsenious oxide is a more trustworthy standard than iodine for volumetric work. Arsenious oxide is non-hygroscopic, and is permanent in both the solid state and in solution. The precautions necessary in the use of both arsenious oxide and iodine are discussed. J. F. S.

An Automatic Burette. GEORGE J. HOUGH (*J. Ind. Eng. Chem.*, 1919, **11**, 229).—The base of the burette consists of a glass tube with an outer jacket, which is passed through an opening in a rubber stopper made to fit into the mouth of the solution bottle. At the side of the jacket is a tube, to which can be attached a rubber pressure bulb, and it also has a side-tube intended to be closed with the finger when air is blown into the bottle. To equalise the pressure, a small hole is provided in the jacket above the level of the liquid in the bottle. When filled, the burette is

closed by a tap at the base, and the solution is drawn off through a side-tubulure ending in a tap. C. A. M.

Chlorine Absorption and Chlorination of Water. ABEL WOLMAN and LINN H. ENSLOW (*J. Ind. Eng. Chem.*, 1919, 11, 209—213).—A series of experiments on different waters to determine the velocity of absorption of available chlorine by the same water during varying intervals of time has shown that the velocity constant, K ($K = 1/t_2 - t_1 \cdot \log N_1/N_2$), decreases, as a rule, with the time of contact. In the case of water containing little organic matter, however, it tends to become constant for different time intervals. The use of colour readings as an index of chlorine absorption is only trustworthy under known conditions with a given water, and the same conclusion applies to the measurement of the turbidity. The chlorine absorption does not increase in direct proportion with the increase in pollution (as measured by oxygen absorption), but shows a decreasing acceleration. The experiments cited appear to indicate that a thirty-minute absorption plus a high factor of safety is unnecessary, and that the addition of a small constant factor to the result, obtained by five minutes' absorption, would be as effective for the routine control of chlorination as the use of a longer time interval. [See also *J. Soc. Chem. Ind.*, 1919, 267A.] C. A. M.

Estimation of Halogens in Organic Compounds. D. VORLÄNDER (*Ber.*, 1919, 52, 308).—The Carius method is unnecessary, except, perhaps, for very volatile substances. The author uses a modification of Baubigny and Chavanne's process (*A.*, 1903, ii, 510; 1904, ii, 203). In the absence of iodine, the substance (about 0.4 gram) is digested with a mixture of mercurous or mercuric nitrate (1 gram), potassium dichromate (6–8 grams), and pure sulphuric acid (40 c.c.) at 130–140°, and the halogen evolved is trapped by a sulphite solution and estimated by Volhard's method. If iodine is present, silver nitrate must be used, when iodic acid is formed.

[For sketch of original apparatus, see *J. Soc. Chem. Ind.*, 1904, 136.] J. C. W.

Apparatus for the Automatic Estimation of Small Amounts of Oxygen in Combustible Gas Mixtures or of Combustible Gases in Air. H. C. GREENWOOD and A. T. S. ZEALLEY (*J. Soc. Chem. Ind.*, 1919, 38, 87–90r).—The apparatus is designed for the purpose of detecting 0.1% or more of oxygen in gas mixtures, and of giving a continuous indication, not necessarily recorded, which will show at any moment the actual concentration. The principle involved is that of the combustion of the oxygen or other impurity by means of an intermittently heated platinum wire; automatic arrangements are provided for making and breaking the required electrical contacts, sealing up the combustion vessel during the heating period, cooling the gas, and

measuring the resulting contraction, ringing an electric bell at a specified oxygen concentration, and flushing out the spent gas by a new charge. A diagram is given of the apparatus, and the original paper should be consulted for details regarding its operation. W. P. S.

Reagent for, and Method of Estimating, Ozone. LOUIS BENOIST (*Compt. rend.*, 1919, **168**, 612—615).—Fluorescein is a very sensitive reagent for the detection of ozone. At a dilution of 1 in 1,000,000, its solution loses its fluorescence in the presence of a trace of ozone, and is decolorised. At a dilution of 1 in 1000, it loses its fluorescence, but the solution remains yellow in colour. This phenomenon is not produced by oxygen, and it requires an enormous excess of nitrous vapours to destroy the fluorescence. Similarly, chlorine, even if present to the extent of three times the weight of fluorescein, and carbon dioxide, if present to the extent of twenty times the weight of fluorescein, do not destroy the fluorescence of a solution of fluorescein diluted to 1 in 1,000,000. Quantitative measurements indicate that the reaction takes place between two molecules of ozone and one molecule of fluorescein. An optical arrangement is described which permits of the detection of fluorescence in a solution diluted to 1 in 1,000,000,000, and thus, using 3 c.c. of such a solution, it is possible to detect and estimate 10^{-9} grams of ozone, which is a much smaller amount than can be detected by starch iodide. W. G.

Estimation of Sulphites and of Sulphur Dioxide in Gaseous Mixtures. PERCY HALLER (*J. Soc. Chem. Ind.*, 1919, **38**, 52—56r).—A trustworthy method for the estimation of sulphites consists in titration with potassium iodate solution strongly acidified with hydrochloric acid. The addition of glycerol (about 5% of the volume of the solution) to sulphite solutions or to sodium hydroxide solution used for absorbing sulphur dioxide prevents any loss due to oxidation of the sulphite by dissolved air, even when the solution is heated. The presence of the glycerol does not interfere with the subsequent titration of the sulphite; the results obtained for sulphur dioxide in gases are much higher than are found when the sulphur dioxide is absorbed in sodium hydroxide solution to which glycerol has not been added. W. P. S.

Estimation of Sulphates in the Presence of Iron. HERMANN KOELSCH (*Chem. Zeit.*, 1919, **43**, 117).—Examination of barium sulphate precipitates obtained in the estimation of sulphates in zinc blends (compare A., 1916, ii, 194) showed that previous removal of iron had little effect on the purity of the barium sulphate as compared with precipitates obtained after the iron had been separated. The principal impurity in the barium sulphate precipitates, in both cases, was barium chloride; it amounted to about 7% of the weight of the precipitate. It is

pointed out that an error may be introduced owing to the reduction of a portion of the sulphate to sulphide during ignition unless care is taken to ensure oxidation. [See, further, *J. Soc. Chem. Ind.*, 1919, May.] W. P. S.

Estimation of Nitrates in Soil by the Phenoldisulphonic Acid Method. H. A. NOYES (*J. Ind. Eng. Chem.*, 1919, 11, 213—218).—Extraction of the soil with cold water under specified conditions removes the whole of the nitrates present, and they may be accurately estimated by the phenoldisulphonic acid method in an aliquot portion of the filtrate. The presence of chlorides does not interfere with the estimation provided that the temperature is kept below that which causes the chlorides and nitrates to react with the dilute sulphuric acid. Organic substances which yield a coloured extract, or iron in the soil, may be removed by adding calcium hydroxide to the soil before the extraction with water. [See, further, *J. Soc. Chem. Ind.*, 1919, 265A.]

C. A. M.

Estimation of Nitro-groups in Organic Compounds by means of Stannous Chloride. J. G. F. DRUCE (*Chem. News*, 1919, 118, 133).—A modification of Young and Swain's method (A., 1898, ii, 186) for estimating nitro-groups by reduction with stannous chloride and titration of the excess of the latter with iodine solution is found to give satisfactory results (compare also Altmann, A., 1901, ii, 475). [See *J. Soc. Chem. Ind.*, 1919, 247A.]

T. H. P.

Solvent Action of Dilute Citric and Nitric Acids on Rock Phosphate. J. A. STENIUS (*J. Ind. Eng. Chem.*, 1919, 11, 224—227).—The amount of phosphorus extracted from rock phosphate by citric acid of 0.2% strength was approximately the same as that extracted by neutral ammonium citrate solution. Variations in the strength of acid and in the amounts of rock phosphate treated had a great influence on the results. Calcium carbonate and other basic substances reduce the solvent action of citric acid, and the addition of the extra quantity of acid equivalent to the basic substance does not eliminate this influence. Extraction with dilute nitric acid (0.06 to 0.015%) removes still greater amounts of phosphorus, and this acid is therefore still less suitable than citric acid for estimating the available phosphorus. Although ammonium citrate solution does not extract all the available phosphorus, yet if used under uniform conditions it affords a test of the effect of any special treatment of rock phosphate. [See, further, *J. Soc. Chem. Ind.*, 1919, 265A.]

C. A. M.

Methods of Glass Analysis, with Special Reference to Boric Acid and the Two Oxides of Arsenic. E. T. ALLEN and E. G. ZIES (*J. Amer. Ceram. Soc.*, 1918, 1, 739—786).—Tervalent and quinquivalent compounds of arsenic in glass may be separated

by heating the glass with hydrofluoric and sulphuric acids, which expel the tervalent arsenic, but leave the whole of the quinquevalent arsenic in the residue.

The quinquevalent arsenic may be estimated by precipitation as a sulphide, which is then oxidised to arsenic acid, reduced by hydriodic acid, and titrated with standard iodine solution, using starch as indicator. The total arsenic is estimated by fusing the glass with sodium carbonate and a little potassium nitrate, and determining the arsenic as just described. The nitre oxidises any arsenious compounds present, and so prevents their volatilisation. Boric acid is preferably estimated by Chapin's method, in which methyl alcohol and anhydrous calcium chloride are added to an acid solution of the fused glass, the methyl borate is distilled, and collected in sodium hydroxide solution. The methyl alcohol is removed from this by evaporation, the solution rendered acid with hydrochloric acid, heated to expel all carbon dioxide, then rendered neutral to *p*-nitrophenol by the addition of sodium hydroxide; mannitol is then added, and the free boric acid is titrated with standard sodium hydroxide. The results are affected by arsenious acid, but this can be avoided by oxidising the latter with hydrogen peroxide, as arsenic acid is inert. Relatively large amounts of fluorides affect the accuracy of the results, but the proportions usually present do not interfere. Special precautions required in the estimation of iron, zinc, lead, barium, and calcium by customary methods are described, and the suggestion is made that when analysing borosilicate glasses, the boric acid should be expelled by treating the residue obtained by evaporation (to separate the silica) with methyl alcohol before proceeding with the customary method of analysis. Attention is directed to the universal presence of hygroscopic moisture in finely powdered glass, and the effect of this on the analytical results. [For details, see *J. Soc. Chem. Ind.*, 1919, 254A.] A. B. S.

Instrument for the Estimation of Small Quantities of Carbon Monoxide in Hydrogen. E. K. RIDGAL and HUGH S. TAYLOR (*Analyst*, 1919, **44**, 89—94).—The method described depends on the preferential catalytic combustion of the carbon monoxide, the carbon dioxide formed being absorbed and estimated by measuring the conductivity of the solution. The gas (hydrogen) under examination enters the apparatus, and is measured by a gauge; it is then mixed with a small quantity of oxygen, obtained by the electrolysis of sodium hydroxide solution between nickel electrodes, and passes to a catalyst chamber. The latter contains a mixture of iron and chromium oxides, and also a small quantity of ceria and thoria, and is heated at 230°; the gases leaving the combustion chamber are passed through an absorption column, through which a current of *N*/200-calcium hydroxide solution flows at regulated speed, and the solution is collected in an electrolytic cell, where the conductivity is measured. [See, further, *J. Soc. Chem. Ind.*, 1919, 252A.] W. P. S.

[**Estimation of Glucinum in Beryl.**] H. COPAUX (*Compt. rend.* 1919, **168**, 610—612).—See this vol., ii, 192.

The Products of the Reaction of Different Metals with Quinosol. N. SCHOORL (*Pharm. Weekblad*, 1919, **56**, 325—328).—Quinosol (the potassium salt of 8-hydroxyquinoline-5-sulphonic acid) gives an extremely delicate reaction with copper salts (Saul and Crawford, A., 1918, ii, 408). The author extends the use of this reagent, or of "superol (8-hydroxyquinoline sulphate), to the detection of arsenic (arsenate), barium, mercury (mercurous), lead, strontium, tin (stannous and stannic), iron (ferrous), and silver. The reagent superol is applied in the form of a 0.2% solution in water. The precipitates produced, except in the case of iron, are microcrystalline and of extremely characteristic appearance. 0.5 Mg. of copper per litre may be detected in this way.

W. S. M.

Estimation of Lead in Lead Salts. R. L. MORRIS (*Chem. and Drug.*, 1919, **91**, 52—54).—The method described in the British Pharmacopœia for the estimation of lead in lead salts (precipitation as oxalate and titration of the precipitate with permanganate solution) yields low results unless the precipitation is made in a solution containing at least 60% of acetic acid. [See, further, *J. Soc. Chem. Ind.*, 1919, 251A.]

W. P. S.

Errors in the Analysis of Chrome Ironstone [Chromite], and a New Process. JAMES MOIR (*J. S. African Assoc. Anal. Chem.*, 1919, **2**, [i], 9—16).—From an investigation made with synthetic mixtures, it is concluded that errors amounting to 10% of the chromium present are quite possible in the analysis of chromite by the usual methods. A modification of the sodium peroxide fusion method is described by which results averaging 99.6% of the truth, with a total variation of about 1%, were obtained. [See, further, *J. Soc. Chem. Ind.*, 1919, 260A.]

W. E. F. P.

o-Tolidine as a Colorimetric Test for Gold. W. B. POLLARD (*Analyst*, 1919, **44**, 94—95).—A 0.1% o-tolidine solution in 10% hydrochloric acid gives a bright yellow coloration with a gold chloride solution containing one part of gold in one million parts of water; the colour can just be detected in a solution containing one part in twenty millions if observed in a depth of 10 cm. of liquid. If free chlorine is present, the coloration requires about three minutes for full development. Ruthenium, iron, osmic acid, and vanadates also give a yellow coloration with the reagent, but other metals do not interfere with the test. In the presence of copper, a green coloration may be obtained instead of a pure yellow. Nitrites and other reducing substances must not be present. [See, further, *J. Soc. Chem. Ind.*, 1919, 269A.]

W. P. S.

The "Dracorubin" and "Dracorubin Capillary" Tests for Identifying and Differentiating Colourless Liquids.

KARL DIETERICH (*Ber. Deut. pharm. Ges.*, 1918, **28**, 449—492).—The test papers employed are prepared by immersing strips of filter paper, 7 cm. long by 1 cm. wide, in an alcoholic or benzene solution of the portion of Sumatra palm resin (palm dragon's blood), which is insoluble in boiling light and heavy petroleum; the strips are dried before use. When these papers are immersed in various organic liquids, the red colouring matter is removed more or less completely, according to the solvent properties of the liquid. The rate of solution, the coloration of the liquid after fifteen minutes and twenty-four hours, respectively, and the appearance of the paper after removal from the liquid, are different in the case of such liquids as alcohol, ether, petroleum, benzene, acetone, turpentine, etc. In the "capillary" test, the paper is suspended so that its lower end dips to a depth of 1 cm. in the liquid. [See, further, *J. Soc. Chem. Ind.*, 1919, 306A.]

W. P. S.

Estimation of Glycerol by means of the Specific Gravity and Boiling Point.

AD. GRÜN and TH. WIRTH (*Zeitsch. angew. Chem.*, 1919, **32**, i, 59—62).—According to various authorities, the specific gravity of pure glycerol varies by 0.0025 to 0.0030 for each 1% of water added, whilst the recorded values for pure glycerol itself vary up to 0.0110, which would correspond with about 3½% of water. The results obtained with samples of pure anhydrous glycerol by the authors were D_4^{20} 1.2653±0.0001, and were thus in agreement with those given by Gerlach (*Chem. Ind.*, 7, 277), whose table must therefore be accepted as the most trustworthy. As was shown by Gerlach (*loc. cit.*), the boiling point of glycerol is lowered from 290° to 239° by the addition of 1% of water. In the determinations made by means of Schleiermacher's apparatus (A., 1891, 873), the boiling point of pure glycerol was found to be 283° to 284°, but this was proved to be due to the absorption of about 0.05% of water during the introduction of the glycerol into the capillary tube. The method affords the most trustworthy means of estimating small amounts of water in glycerol, and is applicable in the presence of organic and inorganic salts, such as sodium chloride, but cannot be used with crude glycerins containing polyglycerols. [See also *J. Soc. Chem. Ind.*, 1919, 295A.]

C. A. M.

Preparation of a Solution of Cupric Hydroxide in Sodium Hydroxide for the Detection and Estimation of Sugars.

ED. JUSTIN-MUELLER (*J. Pharm. Chim.*, 1919, [vii], 19, 18—20).—A solution, which serves all the purposes of Fehling's solution, may be obtained by adding 20 c.c. of 10% copper sulphate solution to 100 c.c. of 33.69% sodium hydroxide solution; the solution remains clear when kept, and does not give a precipitate when heated.

W. P. S.

Analysis of Cows' Milk, Particularly the Estimation of Lactose. HANS SALOMON and RUDOLF DIEHL (*Ber. Deut. pharm. Ges.*, 1918, **28**, 493—498).—Analyses are recorded showing that the quality of cows' milk has not been affected by the poor fodder available lately in Germany. In the estimation of lactose, the preliminary removal of proteins, etc., by precipitation with copper sulphate and sodium hydroxide, is not always complete, especially in the case of milks which have been preserved by the addition of formaldehyde; the use of zinc sulphate, copper sulphate alone, or a mixture of asaprol (sodium β -naphthol- α -monosulphonate) and citric acid is recommended for the purpose. W. P. S.

A New Method for the Estimation of Oxalic Acid. HUGO KRAUSE (*Ber.*, 1919, **52**, [B], 426—432).—When oxalic acid is heated with acetic anhydride at 100°, it decomposes briskly and quantitatively into carbon monoxide and carbon dioxide. Performed in a tube fitted with a generator of carbon dioxide and a nitrometer filled with potassium hydroxide, the reaction may therefore be used for quantitative purposes. The only common organic acid which also gives carbon monoxide under these conditions is formic acid, although even this reacts more sluggishly.

For soluble oxalates, the material is first evaporated with an excess of hydrochloric acid, and the slightly moist residue is spread out on the walls of the tube by shaking during the evaporation. Insoluble oxalates are treated with a mixture of acetic anhydride and sulphuric acid (9:1), but the method is not so good in this case, as the mixture alone develops some insoluble gas, necessitating a "blank" experiment, nor is it specific for oxalic acid.

J. C. W.

Volumetric Method for the Estimation of Salicylic Acid in the Presence of Salicylaldehyde. R. BERG (*Chem. Zeit.*, 1919, **43**, 129).—The method depends on the formation of a yellow coloration when a solution of salicylaldehyde is treated with a slight excess of free alkali; the aldehyde thus acts as an indicator. An ethereal solution containing salicylic acid and salicylaldehyde is extracted with several successive quantities of $N/20$ -sodium hydrogen carbonate solution, and the aqueous extract is titrated with $N/20$ -sulphuric acid, the solution being boiled after each addition of the acid to expel carbon dioxide. The end-point is denoted by the solution remaining colourless when boiled. [See, further, *J. Soc. Chem. Ind.*, 1919, May.] W. P. S.

Volumetric Method for the Estimation of Urea. Applicable to Urine, Blood, Serum, etc. GOLSE (*Bull. Soc. Pharm. Bordeaux*, 1918, **56**, 188; from *J. Pharm. Chim.*, 1919, [vii], **19**, 20—22).—The urea solution is treated with a definite quantity (an excess) of sodium hypobromite solution, and, after one minute, potassium iodide and acetic acid are added and the liberated iodine is titrated with thiosulphate solution. The same

volume of hypobromite solution is then treated separately with potassium iodide and acetic acid, and titrated. The difference between the two titrations is equivalent to the amount of urea present; 6 atoms of iodine correspond with 1 molecule of urea. In the case of urine, the urea is precipitated as a mercury compound by treating the urine with Patein's reagent and sodium hydroxide; the precipitate is collected, washed, dissolved in acetic acid, and the solution treated as described. Blood is clarified with trichloroacetic acid, filtered, the urea precipitated in the filtrate by means of Patein's reagent and sodium hydroxide, and the process continued as above.

W. P. S.

Reduction of the Quantity of Humin Nitrogen Formed in the Hydrolysis of the Nitrogenous Constituents of Feeding-stuffs. H. C. ECKSTEIN and H. S. GRINDLEY (*J. Biol. Chem.*, 1919, **37**, 373—376. Compare A., 1915, ii, 598, and A., 1916, i, 623; ii, 119).—The authors have attempted to render the Van Slyke method for the determination of the chemical groups characteristic of the amino-acids of proteins applicable with greater accuracy than heretofore in the analysis of feeding stuffs. In the first place, the interference of some of the non-protein nitrogenous constituents, such as certain lipoids, pigments, betaines, amygdalin, alkaloids, and some amides has been obviated by completely extracting the food product first with ether and then with cold absolute alcohol. In the second place, a method has been perfected by which the percentages of the humin nitrogen formed in the hydrolysis of the nitrogenous constituents of feeding stuffs are reduced so that they compare favourably with those obtained for pure proteins. This is effected, firstly, by the extraction referred to above, after which insoluble carbohydrates are converted as far as possible into soluble carbohydrates by boiling with 0.1% hydrochloric acid. The greater part of the soluble proteins is separated before hydrolysis from the soluble carbohydrates by neutralising the mineral acid and precipitating with alcohol. The small portion of proteins remaining in solution is hydrolysed by boiling with 5% hydrochloric acid instead of 20%.

By this method, the humin nitrogen is represented by values approximately a third of those obtained by the direct method.

J. C. D.

The Indophenine Reaction. EDWARD WRAY (*J. Soc. Chem. Ind.*, 1919, **38**, 83—84t. Compare A., 1904, i, 337; 1905, ii, 779).—A green coloration instead of blue is obtained in this reaction unless a small quantity of an oxidising substance, preferably nitric acid, is present. The test is made as follows: 25 c.c. of a 0.05% isatin solution in pure sulphuric acid are placed in a stoppered cylinder, and 1 c.c. of the benzene to be tested for thiophen is added, followed by 25 c.c. of sulphuric acid containing one drop of nitric acid; a blue coloration appears when the mixture is shaken.

W. P. S.

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paid us the compliment of copying it as soon as the home manufacture could be arranged. The French considered that the protection it gave was even unnecessarily high.

In the last year of his life Harrison was called on to participate in the offensive side of gas warfare, and to exercise his great organising talent in what had become a very imposing and difficult undertaking. He had now reached the position to which his talents and labours so justly entitled him, but before he could actually officiate as Director of Chemical Warfare, the haunting fear of his friends was realised, and he was prostrated by influenza. His bodily strength, sapped by unceasing labour, was unequal to the strain, pneumonia supervened, and he passed away, as certainly as anyone on the battlefield, a sacrifice of the war. His elder son had fallen in France in 1916.

It is not easy to do justice to Harrison's personal qualities. He was a man of the strongest character. The love of his country, its ideals of freedom, its democratic institutions, and his belief in the destiny of the British as leaders among free peoples were the inspiration of his life and work. He had no thought for himself when the lives of others were at stake. The inflexible sense of duty which animated him communicated itself to those who worked with him, and he gained in a remarkable degree their respect and affection. He faced all emergencies with imperturbability, was never daunted or discouraged, and preserved a clear head and a power of decision even when worn out with incessant labour. He was neither dogmatic nor impatient, but always ready to improve on himself, listening with patience and courtesy to all honest criticism or advice. He was a master organiser, and the War brought him his opportunity. He died acknowledged and revered as a leader of men, his great task accomplished. He was buried with full military honours, mourned by a multitude of fellow-labourers who had learned something of his worth.

Harrison died before he had received the public honours that would undoubtedly have been conferred on him. He had been made C.M.G. in 1917, and the French had shown their appreciation of his services by making him Officer of the Legion of Honour. It is gratifying to know that a memorial to perpetuate his name is to be associated with the Chemical Society. What the nation owes him for the saving of life and the mitigation of suffering can scarcely be overestimated.

A. S.
H. S. R.

XLV.—*Studies on the Dependence of Optical Rotatory Power on Chemical Constitution. Part I. Position-Isomerism and Optical Activity of Naphthyliminocamphors and Derivatives of Phenyliminocamphor.*

By BAWA KARTAR SINGH and JATINDRA KUMAR MAZUMDER.

THE relation between chemical constitution and rotatory power which is investigated in the present paper is that of position-isomerism in the aromatic groups present in optically active derivatives of phenyliminocamphor.

Frankland in 1896 (T., 69, 1583) suggested a theory to explain the changes in rotatory power produced by nuclear substitution in the ortho-, meta-, and para-position in a side-chain containing an active group.

Taking the analogy of a weight acting at the end of a lever arm, he suggested, for reasons based on the relative position of the centre of gravity of the unsubstituted aromatic nucleus on the one hand, and those of the isomeric disubstituted derivatives on the other, that the order of rotatory power should be:

Ortho < unsubstituted nucleus < meta < para.

The line of argument adopted was as follows:

The centre of gravity of the unsubstituted nucleus being at the centre of a regular hexagon, that in the ortho-substituted derivative would be somewhat nearer, in the meta-derivative somewhat further, and in the para-derivative still further than that geometrical centre from the side-chain containing the optically active group.

If, then, the optical activity is determined by the moment of the mass of the group, the rotatory power of the para-compound should be the greatest, that of the ortho-compound the least, and that of the meta-derivative intermediate between those of the other two. In the case of the unsubstituted nucleus, the mass is smaller, but it acts through a longer arm than in the case of the larger mass of the ortho-compound, but through a shorter arm than in either the meta- or the para-compound.

In his Presidential Address to the Chemical Society (T., 1912, 101, 654), Frankland revived this theory, and illustrated its validity by several observations of Cohen and his collaborators. A number of other observations (Cohen, T., 1903, 83, 1214;

T., 1904, **85**, 1271; T., 1905, **87**, 1190; T., 1911, **99**, 1058), however, do not support the rule.

The aim of the present work is to afford evidence in support or in refutation of Frankland's rule from observations made in several series of new compounds. If the theory were correct, that is, if the rotatory power were determined by the position of the centre of gravity of the nucleus in relation to the active group, we should expect: (1) that the greater the mass of the substituting group or element, the greater would be the observed differences between the constants of the para- and ortho-isomerides, and (2) that the para-isomeride would have the maximum rotation.

The molecular rotatory powers of derivatives of phenyliminocamphor are tabulated below.

TABLE I.

| Derivatives of phenyliminocamphor. | [M] _D in chloroform solution. | | | |
|---------------------------------------|---|---------|-----------|-------------------------|
| | -CH ₃ (15) | -Br(80) | -Cl(35.5) | -O-CH ₃ (31) |
| Ortho- | +1183° | +1382° | +441.7° | +612° |
| Meta- | 1665 | 1338 | 1338 | — |
| Para- | 2177 | 1695 | 1768 (a) | 3314 (a) |

The value of [M]_D of phenyliminocamphor is 1750° (Forster and Thornley, T., 1909, **95**, 944).

TABLE II.

| Derivatives of phenylimino- camphor. | [M] _D in methyl alcohol. | | |
|--|-------------------------------------|---------|-----------|
| | -CH ₃ (15) | -Br(80) | -Cl(35.5) |
| Ortho- | +1030° | +1311° | +486.4° |
| Meta- | 1504 | 1260 | 1261 |
| Para- | 2001 | 1545 | — |

The value of [M]_D for phenyliminocamphor in methyl alcohol solution is 1462°.

The mean temperature of observations recorded in tables I and II was 26° to 32°.

It will now be seen that in no case is Frankland's rule borne out by the results recorded in tables I and II. In the case of the tolyl and chlorophenyl derivatives, the value of the rotatory power for the unsubstituted compound (namely, phenyliminocamphor) lies between that for the meta- and para-derivative, and is therefore in opposition to Frankland's rule. The order of rotatory powers in the case of the bromophenyl derivatives in chloroform is meta < ortho < para < unsubstituted compound, and here deviation from Frankland's rule is seen to be most marked.

Although the mass of the group (CH_3) in the case of the tolyl compounds is less than that in the case of the bromophenyl derivatives (Br), the observed difference in the values of the rotatory powers of the ortho- and para-isomerides is more than three times as high in the former as in the case of the latter. This result is again contrary to what we should expect if Frankland's rule were valid.

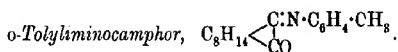
The para-isomeride has in all the above cases, except in the case of the bromophenyl derivative, the maximum rotation, and this is in accordance with the deduction made from Frankland's rule.

It is thus clear that the results recorded in the present paper do not generally support Frankland's rule. Only in one direction can we say that Frankland's theory has been supported, namely, that the ortho-compound has the least and the para-derivative the maximum rotation (except in one instance).

Cohen, as the result of his observations (T., 1910, **97**, 1737; 1911, **99**, 1060), lays down the following rule: The rotatory effect of the ortho-grouping differs more from that of the phenyl than do those of meta- and para-groupings. A glance at tables I and II will show that this rule is also not supported. In the case of the bromophenyl derivatives, it is the meta, and in the case of the methoxyphenyl derivatives it is the para, and not the ortho, which differs more in rotation from the value of the unsubstituted compound.

Further, no simple connexion can be observed between the nature of the substituting element or group in an optically active compound and its rotatory power. In the case of ortho-compounds (table I), it is seen that the order of elements or groups with increasing rotation is $\text{Cl} < \text{O}\cdot\text{CH}_3 < \text{CH}_3 < \text{Br} < \text{H}$, in the case of meta-compounds $\text{Cl} = \text{Br} < \text{CH}_3 < \text{H}$, and in the case of para-compounds $\text{Br} < \text{H} < \text{Cl} < \text{CH}_3 < \text{O}\cdot\text{CH}_3$.

EXPERIMENTAL.



Camphorquinone and *o*-toluidine in molecular proportion were heated with anhydrous sodium sulphate for several hours on the water-bath. On cooling, water was added, when a solid substance was precipitated, which crystallised from 50 per cent. alcohol in yellow prisms melting at $120\text{--}121^\circ$.

It is very readily soluble in chloroform, ether, benzene, or acetone, less so in methyl or ethyl alcohol, and insoluble in water:

0.2074 gave 10.6 c.c. N_2 at 30° and 759.5 mm. $N=5.78$.

$C_{17}H_{21}ON$ requires $N=5.49$ per cent.

The following determinations of rotatory power were made by dissolving the given weight of substance in 19.9 c.c. of the solvent, and the first observation was made within half an hour of making up the solution. This applies to all the observations, unless the contrary is stated. The length of the tube was 2-dcm.

| Solvent. | Substance. Gram. | Tem- perature. | Time hours. | α_D . | $[\alpha]_D$. | $[M]_D$. |
|---------------------|---------------------|-------------------|----------------|---------------|----------------|---------------|
| Chloroform | 0.1470 | 32° | — | $+6.85^\circ$ | $+464.1^\circ$ | $+1183^\circ$ |
| | | | 19 | 6.86 | 464.4 | 1184 |
| Methyl alcohol..... | 0.1519 | 34 | — | 6.16 | 403.6 | 1030 |
| „ | „ | „ | 21 | 6.08 | 398.4 | 1016 |

m-Tolyliminocamphor.

Molecular proportions of camphorquinone and *m*-toluidine, mixed with a little fused sodium sulphate, were heated on the water-bath for five hours. The product was cooled and dissolved in a small quantity of alcohol; water was added, when an oil separated which solidified on keeping. The substance was crystallised from dilute (50 per cent.) alcohol in yellow prisms melting at $85-86^\circ$.

It is very readily soluble in methyl or ethyl alcohol, chloroform, ether, or acetic acid, and insoluble in water:

0.1425 gave 7.6 c.c. N_2 at 31° and 760 mm. $N=5.9$.

$C_{17}H_{21}ON$ requires $N=5.49$ per cent.

The rotatory power determinations gave the following values:

| Solvent. | Substance. Gram. | Tem- perature. | Time in hours. | α_D . | $[\alpha]_D$. | $[M]_D$. |
|--------------------|---------------------|-------------------|-------------------|---------------|----------------|---------------|
| (a) Chloroform ... | 0.0649 | 31° | — | $+4.26^\circ$ | $+653.0^\circ$ | $+1665^\circ$ |
| „ ... | „ | 29.5 | 20 | 4.31 | 660.7 | 1684 |
| (b) „ ... | 0.0915 | 17—18 | — | 6.04 | 656.7 | 1675 |
| Methyl alcohol | 0.0903* | 31.0 | — | 5.35 | 589.7 | 1504 |
| „ | „ | 29.5 | $13\frac{1}{2}$ | 5.35 | 589.7 | 1504 |

p-Tolyliminocamphor.

An alcoholic solution of camphorquinone was mixed with a similar solution of *p*-toluidine (in molecular proportion), a little anhydrous sodium sulphate added, and the solution was heated on the water-bath under reflux for three hours.* After evaporating off the alcohol, the residue was poured into water, when a yellow substance separated, which crystallised from dilute alcohol (50 per cent.) in yellow prisms melting at $121-122^\circ$. It is very readily soluble in chloroform, acetone, ether, or benzene, less so in methyl or ethyl alcohol, and insoluble in water:

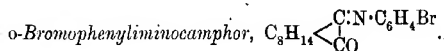
0.2118 gave 10.6 c.c. N_2 at 29° and 764 mm. $N=5.71$.

$C_{17}H_{21}ON$ requires $N=5.49$ per cent.

The rotatory power determinations gave the following values:

| Solvent. * | Substance. Gram. | Tem- perature. | Time in hours. | α_D . | $[\alpha]_D$. | $[M]_D$. |
|---------------------|---------------------|-------------------|-------------------|----------------|----------------|---------------|
| Chloroform | 0.1691 | 28.0° | — | $+14.51^\circ$ | $+853.9^\circ$ | $+2177^\circ$ |
| Methyl alcohol..... | 0.1583 | 29.0 | — | 12.48 | 784.5 | 2001 |
| " | " | 29.0 | 48 | 11.95 | 694.5 | 1771 |
| " | " | 30.5 | 76 | 10.2 | 641.1 | 1634.8 |
| " | " | 29.5 | 142 | 8.79 | 552.6 | 1409 |
| " | " | 30.5 | 166 | 8.26 | 519.2 | 1324 |
| " | " | 30.0 | 219 | 7.55 | 474.5 | 1210 |

The substance when recovered from the polarimeter tube by evaporation to dryness on the water-bath melts at about 110° .



Camphorquinone was added to the calculated quantity of *o*-bromoaniline and a little anhydrous sodium sulphate, the mixture being heated on the water-bath for five hours, cooled, and then dissolved in alcohol. The alcoholic solution on dilution with water furnished an oil, which became solid on keeping for two or three days, and crystallised from dilute alcohol (50 per cent.) in yellow needles melting at 110° .

It is very readily soluble in methyl or ethyl alcohol, chloroform, ether, or acetic acid, and insoluble in water:

C 1109 gave 4.6 c.c. N_2 at 33° and 761 mm. $N=4.65$.

$C_{16}H_{18}ONBr$ requires $N=4.4$ per cent.

The rotatory power determinations gave the following values:

| Solvent. | Substance. Gram. | Tem- perature. | Time in hours. | α_D . | $[\alpha]_D$. | $[M]_D$. |
|---------------------|---------------------|-------------------|-------------------|---------------|----------------|---------------|
| Chloroform | 0.0380 | 32.0° | — | $+1.65^\circ$ | $+432.1^\circ$ | $+1382^\circ$ |
| " | " | 31.0 | 14½ | 1.64 | 429.4 | 1374 |
| Methyl alcohol..... | 0.0362 | 31.0 | — | 1.49 | 409.6 | 1311 |
| " | " | 31.5 | 20½ | 1.19 | 327.2 | 1047 |

m-Bromophenyliminocamphor.

Camphorquinone and *m*-bromoaniline were heated together in the presence of a little anhydrous sodium sulphate on the water-bath for four hours. On cooling, the product was dissolved in alcohol and precipitated by the addition of water. It crystallised from dilute alcohol (50 per cent.) in yellow prisms melting at 116 — 118° , which were very readily soluble in methyl or ethyl alcohol, chloroform, ether, or acetic acid, and insoluble in water:

0.1085 gave 0.0638 AgBr. Br=25.0.

$C_{10}H_{18}ONBr$ requires Br=25.0 per cent.

The rotatory power determinations gave the following values:

| Solvent. | Substance. Gram. | Tem- perature. | Time in hours. | α_D . | $[\alpha]_D$. | $[M]_D$. |
|---------------------|---------------------|-------------------|-------------------|--------------|----------------|-----------|
| Chloroform | 0.1392 | 31° | — | +5.85° | +418.3° | +1338° |
| " | " | 31 | 7½ | 5.81 | 415.5 | 1329 |
| Methyl alcohol..... | 0.1461 | 31 | — | 5.78 | 393.9 | 1260 |
| " | " | 31 | 5 | 5.52 | 376.2 | 1204 |
| " | " | 31 | 22 | 4.94 | 336.7 | 1077 |

The substance when recovered from methyl-alcoholic solution after the last observation by evaporating to dryness on the water-bath melted at 113—114°. A mixture with the original substance melted at 116—118°. It is therefore obvious that the substance undergoes mutarotation in methyl-alcoholic solution, and not in chloroform solution.

p-Bromophenyliminocamphor.

Camphorquinone and *p*-bromoaniline were mixed together in equal quantities. The reaction began at the ordinary temperature, as the mixture became liquid within a short time. After heating for four hours on the water-bath, the reaction was complete. On cooling, the product solidified, and crystallised from dilute alcohol (50 per cent.) in yellow needles melting at 138—139°. The substance is very readily soluble in methyl or ethyl alcohol, chloroform, ether, or acetic acid, and insoluble in water:

0.0750 gave 3.2 c.c. N_2 at 35° and 759 mm. N=4.74.

$C_{16}H_{18}ONBr$ requires N=4.4 per cent.

The rotatory power determinations gave the following values:

| Solvent. | Substance. Gram. | Tem- perature. | Time in hours. | α_D . | $[\alpha]_D$. | $[M]_D$. |
|-------------------|---------------------|-------------------|-------------------|--------------|----------------|-----------|
| Chloroform | 0.1217 | 31° | — | +6.48° | +529.9° | +1695° |
| " | " | 30 | 20 | 6.53 | 534.0 | 1709 |
| Methyl alcohol... | 0.1193 | 31 | — | 5.79 | 483.0 | 1545 |
| " | " | 30 | 22 | 4.31 | 359.5 | 1150 |
| " | " | 30 | 46 | 3.36 | 280.2 | 896.6 |

The substance when recovered from methyl-alcoholic solution after the last observation, by evaporation to dryness, melted at 112—118°, a mixture with the original substance melting at 115—122°. It is clear that the substance exhibits mutarotation in methyl alcohol, but not in chloroform.



Camphorquinone and *o*-chloroaniline were condensed with the aid of a little sodium sulphate by heating on the water-bath for five hours. On allowing to cool, the substance solidified, and crystallised from dilute alcohol (50 per cent.) in silky, yellow needles melting at 128°.

It is very readily soluble in methyl or ethyl alcohol, chloroform, ether, or acetic acid, but sparingly so in water:

0.1233 gave 5.6 c.c. N₂ at 28° and 758 mm. N=5.16.

C₁₆H₁₈ONCl requires N=5.1 per cent.

The rotatory power determinations gave the following values:

| | Solvent. | Substance. Gram. | Tem- perature. | Time in hours. | α_D . | $[\alpha]_D$. | $[M]_D$. |
|-----|----------------|---------------------|-------------------|-------------------|--------------|----------------|-----------|
| (a) | Chloroform ... | 0.0633 | 27.5° | — | +1.02° | +160.4° | +441.7° |
| | " ... | " | 28.0 | 8 | 1.03 | 161.9 | 446.0 |
| (b) | " ... | 0.0994 | 30.0 | — | 1.54 | 154.1 | 424.6 |
| | " ... | (2nd prepn.) | 31.0 | 7½ | 1.54 | 154.1 | 424.6 |
| | Methyl alcohol | 0.0941 | 30.0 | — | 1.67 | 176.6 | 486.4 |
| | " | " | 31.0 | 6½ | 1.67 | 176.6 | 486.6 |

m-Chlorophenyliminocamphor.

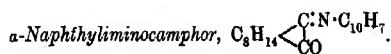
Molecular proportions of camphorquinone and *m*-chloroaniline were condensed with the aid of anhydrous sodium sulphate by heating on the water-bath for four hours. The product was cooled, dissolved in alcohol, and precipitated by the addition of water as a crystalline substance. On recrystallisation from dilute alcohol, pale yellow needles melting at 123—124° were obtained. The substance is very readily soluble in methyl or ethyl alcohol, chloroform, ether, or acetic acid, and insoluble in water:

0.1300 gave 6.2 c.c. N₂ at 32° and 758 mm. N=5.35.

C₁₆H₁₈ONCl requires N=5.1 per cent.

The rotatory power determinations gave the following values:

| Solvent. | Substance. Gram. | Tem- perature. | Time in hours. | α_D . | $[\alpha]_D$. | $[M]_D$. |
|---------------------|---------------------|-------------------|-------------------|--------------|----------------|-----------|
| Chloroform | 0.0666 | 28.0° | — | +3.25° | +485.7° | +1338° |
| | | 27.5 | 24 | 3.19 | 476.7 | 1313 |
| Methyl alcohol..... | 0.0800 | 27.5 | — | 3.68 | 457.7 | 1261 |
| | | 26.5 | 20 | 3.69 | 459.0 | 1264 |



When molecular proportions of camphorquinone and α -naphthylamine were mixed, the mixture soon became liquid at the ordinary temperature. It was heated on the water-bath for four hours to complete the reaction. On cooling, the product was dissolved in alcohol and precipitated by the addition of water, when a solid substance separated which crystallised from dilute alcohol in yellow needles melting at 155° .

It is very readily soluble in methyl or ethyl alcohol, chloroform, ether, or acetic acid, and insoluble in water:

0.1220 gave 5.1 c.c. N_2 at 33° and 759 mm. $N=4.7$.

$C_{20}H_{21}ON$ requires $N=4.8$ per cent.

The rotatory power determinations gave the following values:

| Solvent. | Substance. Gram. | Tem- perature. | Time in hours. | a_D . | $[\alpha]_D$. | $[M]_D$. |
|---------------------|---------------------|-------------------|-------------------|---------------|----------------|-----------|
| Chloroform | 0.0676 | 31.5° | — | $+4.14^\circ$ | $+809.6^\circ$ | $+1774^*$ |
| | " | 32.0 | $9\frac{1}{2}$ | 4.14 | 809.6 | 1774 |
| Methyl alcohol..... | 0.1199 | 31.5 | — | 6.73 | 558.5 | 1625 |
| " | " | 32.0 | $7\frac{1}{2}$ | 6.73 | 558.5 | 1625 |

The substance does not exhibit any mutarotation.

β -Naphthyliminocamphor.

Camphorquinone and β -naphthylamine were condensed in molecular proportions by heating on the water-bath for four hours. The substance on crystallisation from dilute alcohol in the usual manner gave yellow needles melting at 140 — 142° .

These are very readily soluble in methyl or ethyl alcohol, acetic acid, ether, or chloroform, and insoluble in water:

0.1100 gave 4.6 c.c. N_2 at 32° and 760 mm. $N=4.4$.

$C_{20}H_{21}ON$ requires $N=4.8$ per cent.

The rotatory power determinations gave the following values:

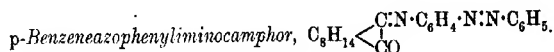
| Solvent. | Substance. Gram. | Tem- perature. | Time in hours. | a_D . | $[\alpha]_D$. | $[M]_D$. |
|---------------------|---------------------|-------------------|-------------------|---------------|----------------|-----------|
| Chloroform | 0.0966 | 32° | — | $+6.62^\circ$ | $+682.0$ | $+1985^*$ |
| | " | 31 | 15 | 6.66 | 686.0 | 1996 |
| Methyl alcohol..... | 0.1140 | 31 | — | 7.45 | 650.5 | 1893 |
| " | " | 31 | $10\frac{1}{2}$ | 7.35 | 641.6 | 1867 |

Phenyliminocamphor.

This substance was prepared according to Forster's method (T., 1909, **95**, 949), and formed silky, yellow needles melting at 110 — 112° .

The rotatory power determinations gave the following values :

| Solvent. | Substance. Gram. | Tem- perature. | Time in hours. | α_D . | $[\alpha]_D$. | $[M]_D$. |
|---------------------|---------------------|-------------------|-------------------|--------------|----------------|-----------|
| Methyl alcohol..... | 0.0920 | 26.5° | — | +5.61° | +606.8° | +1462° |
| " | " | 27.0 | 27 | 5.51 | 596.1 | 1437 |



Camphorquinone and aminoazobenzene, in molecular proportions, were heated on the water-bath for six hours. The product was cooled, dissolved in alcohol, and precipitated as an oil by the addition of water. The oil, on keeping for two days, solidified. It crystallised from dilute alcohol in orange needles melting and decomposing at 129—130°.

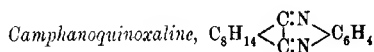
The substance is very readily soluble in methyl or ethyl alcohol, chloroform, ether, or acetic acid, and insoluble in water :

0.1140 gave 12.5 c.c. N_2 at 32° and 759 mm. $N=12.5$.

$C_{22}H_{23}ON_3$ requires $N=12.36$ per cent.

The rotatory power determinations gave the following values :

| Solvent. | Substance. Gram. | Tem- perature. | Time in hours. | α_D . | $[\alpha]_D$. | $[M]_D$. |
|---------------------|---------------------|-------------------|-------------------|--------------|----------------|-----------|
| Chloroform | 0.0557 | 23.0° | — | +3.08° | +550.4° | +1899° |
| " | " | 23.5 | 22 | 3.25 | 580.8 | 2004 |
| Methyl alcohol..... | 0.0359 | 24.0 | — | 2.06 | 571.1 | 1970 |
| " | " | 24.5 | 22 | 2.05 | 568.4 | 1961 |



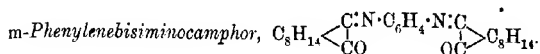
The quinoxaline derivative is obtained quantitatively by heating on the water-bath alcoholic solutions of camphorquinone and *o*-phenylenediamine. On dilution with water, it separates as an oil, which on rubbing becomes pasty and then solidifies. It is purified by dissolving in alcohol and precipitating with water, being obtained as a white, amorphous substance melting at 77—78°. It is very readily soluble in methyl or ethyl alcohol, acetone, glacial acetic acid, ether, benzene, light petroleum, carbon disulphide, or chloroform, and insoluble in water :

0.1725 gave 18.55 c.c. N_2 at 30.5° and 759.5 mm. $N=12.1$.

$C_{18}H_{18}N_2$ requires $N=11.76$ per cent.

The rotatory power determinations gave the following values :

| Solvent. | Substance. Gram. | Tem- perature. | Time in hours. | α_D . | $[\alpha]_D$. | $[M]_D$. |
|----------------------|---------------------|-------------------|-------------------|--------------|----------------|-----------|
| Ethyl alcohol | 0.2980 | 23.5° | — | +0.97° | +32.4° | +77.1° |
| " | " | 24.0 | 8½ | 0.94 | 31.4 | 74.71 |
| " | " | 23.0 | 23½ | 0.94 | 31.4 | 74.71 |
| Chloroform | 0.3979 | 28.0 | — | 1.14 | 28.51 | 67.86 |
| " | " | 27.0 | 18 | 1.17 | 29.26 | 69.65 |
| Methyl alcohol | 0.4254 | 30.0 | — | 1.43 | 33.45 | 79.6 |



An alcoholic solution of camphorquinone (2 mols.) was added to an aqueous solution of *m*-phenylenediamine hydrochloride mixed with excess of sodium acetate, and heated for half an hour on the water-bath. The condensation product was obtained as an oil, which solidified on keeping and crystallised from dilute alcohol in yellow needles melting at 150—151°.

It is very readily soluble in methyl or ethyl alcohol, acetic acid, chloroform, ether, or pyridine, and insoluble in water:

0.1300 gave 8.25 c.c. N_2 at 31° and 760 mm. $\text{N} = 7.16$.

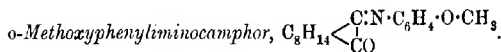
$\text{C}_{26}\text{H}_{32}\text{O}_2\text{N}_2$ requires $\text{N} = 6.93$ per cent.

The same substance was also obtained when camphorquinone and *m*-phenylenediamine were condensed in molecular proportions.

The rotatory power determinations gave the following values:

| Solvent. | Substance. Gram. | Tem- perature. | Time in hours. | α_D . | $[\alpha]_D$. | $[M]_D$. |
|----------------------|---------------------|-------------------|-------------------|--------------|----------------|-----------|
| Methyl alcohol | 0.0193 | 30.5° | — | +1.23° | +634.1° | +2563° |
| Chloroform | 0.0395 | 29.0 | — | 0.52 | 658.3 | 2660 |
| " | (in 100 c.c.) | 28.0 | 21 | 0.53 | 671.0 | 2710 |

More concentrated solutions were too dark for observations to be made on them.



Camphorquinone and *o*-anisidine were mixed in molecular proportions, a little anhydrous sodium sulphate was added, and the whole heated on the water-bath for four hours. On cooling the product, it was dissolved in alcohol and precipitated by water. It crystallised from dilute alcohol in pale yellow prisms melting at 125—126°.

The substance is very readily soluble in methyl or ethyl alcohol, chloroform, ether, or acetic acid, and insoluble in water:

0.1135 gave 5.6 c.c. N_2 at 28° and 759 mm. $\text{N} = 5.61$.

$\text{C}_{17}\text{H}_{21}\text{O}_2\text{N}$ requires $\text{N} = 5.2$ per cent.

The rotatory power determinations gave the following values. The solution was somewhat dark, and therefore difficult to read:

| Solvent. | Substance. Gram. | Tem- perature. | Time in hours. | α_D . | $[\alpha]_D$. | $[M]_D$. |
|------------------|---------------------|-------------------|-------------------|--------------|----------------|-----------|
| Chloroform | 0.0639 | 27° | — | +1.45° | +225.8° | +612.0° |
| " | " | 28 | 27, | 1.47 | 228.9 | 620.3 |

Condensations between camphorquinone and *m*-nitro-*p*-toluidine, *o*-, *m*-, and *p*-aminobenzoic acids, could not be effected.

This work was carried out at Dacca College. It is now being continued at Government College, Lahore.

THE CHEMICAL LABORATORY,
GOVERNMENT COLLEGE,
LAHORE, PUNJAB, INDIA.

[Received, January 13th, 1919.]

XLVI.—The Nitration of Diphenylethylenediamine.

By GEORGE MACDONALD BENNETT.

It was shown by Mills in 1900 (T., 77, 1020) that diphenylethylenediamine, $C_6H_5 \cdot NH \cdot CH_2 \cdot CH_2 \cdot NH \cdot C_6H_5$, may be nitrated in glacial acetic acid solution with the production of two isomeric tetranitro-derivatives, one melting at 303°, the other at 85°, the latter being much the more readily soluble in various solvents, and easily converted into the former by boiling its solution in acetone.

The close relationship between diphenylethylenediamine and monomethylaniline made it probable that an octanitro-derivative of the former might be obtained, analogous to trinitrophenylmethylnitroamine, $C_6H_2(NO_2)_3 \cdot NMe \cdot NO_2$. This proved to be the case, and the expected hexanitrodiphenylethylenedinitroamine, $[C_6H_2(NO_2)_3 \cdot N(NO_2) \cdot CH_2]_2$, was isolated, either by nitrating the base in sulphuric acid, using a large excess of fuming nitric acid, or by using little more than the theoretical amount of nitric acid in the presence of fuming sulphuric acid.

From the products of the reaction there was also isolated a small quantity of a hexanitro-derivative, which must be isomeric with the compound melting at 230° obtained by Jedlicka (*J. pr. Chem.*, 1893, [ii], 48, 204) by the interaction of ethylenediamine and either trinitroanisole or picryl chloride. This new hexanitrodiphenylethylenediamine and the Mills's tetranitro-compound (m. p. 85°), which it resembles closely in properties, are probably tetra- and di-nitrodiphenylethylenedinitroamines.

EXPERIMENTAL.

Preparation of Diphenylethylenediamine.

The base has hitherto been prepared by the interaction of aniline and ethylene dibromide (Morley, *Ber.*, 1879, 12, 1794), but it may be equally readily obtained by using the dichloride, the mixture of the latter with four molecular proportions of aniline being boiled for three-quarters of an hour. The reaction is much less violent than with the bromide. The base may be conveniently purified in the form of its *sulphate*, $C_{14}H_{16}N_2 \cdot H_2SO_4 \cdot H_2O$, which crystallises from hot water in colourless needles, being sparingly soluble in the cold:

1.502 (air-dried) lost in a vacuum 0.079. $H_2O = 5.3$.

$C_{14}H_{16}N_2 \cdot H_2SO_4 \cdot H_2O$ requires $H_2O = 5.8$ per cent.

0.3914 required 23.98 c.c. $N/10$ -NaOH. Calc., 23.86 c.c.

2:4:6:2':4':6'-Hexanitrodiphenylethylenedinitroamine.

Fifteen grams of the sulphate (dried at 110°) were dissolved in 100 grams of sulphuric acid (97 per cent.), and the solution was run slowly into 60 c.c. of fuming nitric acid (D 1.52) kept vigorously stirred at $30-35^\circ$. The temperature of the mixture was then slowly raised, and kept finally at 80° during an hour. When the product was cold, the solid which had been precipitated was collected on asbestos and washed successively with dilute sulphuric acid (70 per cent.), water, sodium carbonate solution, and finally with water. There remained, after drying, 19 grams of a yellow, sandy powder which melted and decomposed at 200° . A similar result was obtained when the nitration was carried out in the presence of fuming sulphuric acid, using the calculated amount (eight molecular proportions) of nitric acid. By washing the sandy product with ethyl acetate or, better, by recrystallisation from acetone, in which it is sparingly soluble, the octanitro-derivative was obtained as a pale yellow, crystalline powder melting and decomposing at 213° (uncorr.):

0.2771 gave 0.2974 CO_2 and 0.0400 H_2O . $C = 29.3$; $H = 1.61$.

0.1315 „ 26.75 c.c. N_2 (moist) at 15° and 763 mm.

$N = 24.03$.

$C_{14}H_8O_{10}N_{10}$ requires $C = 29.3$; $H = 1.4$; $N = 24.5$ per cent.

This compound is insoluble in the ordinary organic solvents, with the exception of ethyl acetate and acetone, in which it is appreciably soluble. It may be obtained in minute, lemon-yellow crystals

by crystallisation from nitrobenzene, in which it is readily soluble. It explodes on sudden heating. When heated with a concentrated solution of sodium hydroxide, it is decomposed, with the formation of picric acid.

Hexanitro-derivative.

The dark-coloured mother liquors from the purification of the crude octanitro-derivative by means of ethyl acetate or acetone left, on evaporation, a dark brown powder which appeared to be a mixture, and from which crystalline products could not readily be isolated. By fractional precipitation of its solution in glacial acetic acid by the addition of water, an amorphous, canary-yellow powder was obtained which melted and decomposed at 70° , and appeared to be a hexanitro-derivative:

0.1834 gave 0.2362 CO_2 and 0.0413 H_2O . $\text{C}=34.6$; $\text{H}=2.5$.

$\text{C}_{14}\text{H}_{10}\text{O}_{12}\text{N}_8$ requires $\text{C}=34.8$; $\text{H}=2.07$ per cent.

It is readily soluble in acetone, glacial acetic acid, ethyl acetate, or nitrobenzene, but practically insoluble in chloroform, benzene, carbon tetrachloride, or light petroleum.

This investigation was carried out during 1915 in the Cambridge University laboratories at the suggestion of Prof. Sir William Pope, to whom the author's best thanks are due.

50, CITY ROAD, E.C. 1.

[Received, May 2nd, 1919.]

XLVII.—*The Propagation of Flame in Mixtures of Acetylene and Air.*

By WALTER MASON and RICHARD VERNON WHEELER.

MEASUREMENTS of the speed of the "uniform movement" during the horizontal propagation of flame in mixtures of acetylene and air have recently been made by Haward and Sastry (T., 1917, 111, 841) in revision of earlier determinations by Le Chatelier (*Compt. rend.*, 1895, 121, 1144).

The electrical method of measuring the speeds of the flames employed by Haward and Sastry was found by them to be unsatisfactory when the propagation took place in a tube of as large a diameter as 25 mm., the duration of the uniform movement being too short and its speed too great to allow of sufficiently

accurate records being obtained. For this reason, they reported only results procured by using a tube 12 mm. in diameter. The tube employed by Le Chatelier was 40 mm. in diameter.

The maximum speeds during the uniform movement were found to be with mixtures containing from 8 to 10 per cent. of acetylene, and were: in a 12-mm. tube (Haward and Sastry), 260 cm. per second; in a 40-mm. tube (Le Chatelier), about 600 cm. per second.

From the results obtained with inflammable gases other than acetylene (see, for example, T., 1917, 111, 1044), one would not expect to find the speed of the uniform movement of flame so dependent on the diameter as these figures indicate. Means were therefore sought to compare the speeds in tubes of different diameters. From the appearance of the flames, it seemed probable that they would have sufficient actinic power to affect a sensitive photographic film during quite a short time of exposure, so that it should be possible to employ the photographic method of recording the speeds of flames devised by Mallard and Le Chatelier (*Ann. des Mines*, 1883, [viii], 4, 312) for use with mixtures of carbon disulphide with oxygen or nitric oxide, the flames of which are highly actinic. On trial, it was found that over the whole range of inflammable mixtures of acetylene and air a sufficiently definite image of the flame was obtained on a highly sensitive photographic film moving at a rapid speed in a direction normal to the direction of propagation of flame.

This method, described in detail in the experimental portion of this paper, was therefore adopted for the determinations of the speeds of the uniform movement of flame in mixtures of acetylene and air herein recorded, tubes 12.5, 25, 50, and 90 mm. in diameter being used.

Apart from its value in enabling the mean speed of propagation of flame over a measured distance to be calculated, the photographic method enables a detailed study to be made of the manner of movement of the flame. Such a study has been made, with particular reference to the phenomena resulting in and accompanying the detonation wave, by Dixon (*Phil. Trans.*, 1903, [A], 200, 315), who has brought flame "analysis" by these means to the acme of perfection.

Mallard and Le Chatelier's observations on the mode of propagation of flame, as revealed by photographs, have frequently been epitomised; but it is desirable to recall them again, preferably in Le Chatelier's words, which are as follow ("Le Carbone," p. 273; Paris, 1908):

"On constate dans ces conditions, lorsque l'inflammation a été mise du côté de l'extrémité ouverte du tube, que la flamme se

propage d'abord avec une vitesse sensiblement uniforme; la courbe enregistrée est alors une droite, plus ou moins inclinée; il se développe bientôt des mouvements vibratoires dans la masse gazeuse qui prennent parfois une violence extraordinaire, la courbe présente des ondulations très accentuées; enfin, dans certains cas, la propagation de l'inflammation devient brusquement, en quelque sorte, instantanée, du moins tellement rapide qu'il est bien difficile de reconnaître l'existence d'une vitesse définie."

This description is founded mainly on the results of experiments with mixtures of carbon disulphide and nitric oxide, for with no other inflammable gas was the flame sufficiently rich in actinic rays to affect satisfactorily the rapidly moving sensitised paper (gelatino-bromide paper) which Mallard and Le Chatelier used. The description is, however, intended to apply to the propagation of flame in most gaseous mixtures ignited under the conditions specified.

It will be understood that an advantage of this method of determining the speed of uniform movement of flame, over such as involve the fusion of screen-wires at fixed positions along its path, lies in the assurance given by the photograph that no part of the "vibratory movement," during which the flame may momentarily attain a very rapid speed, is included in the measurement.

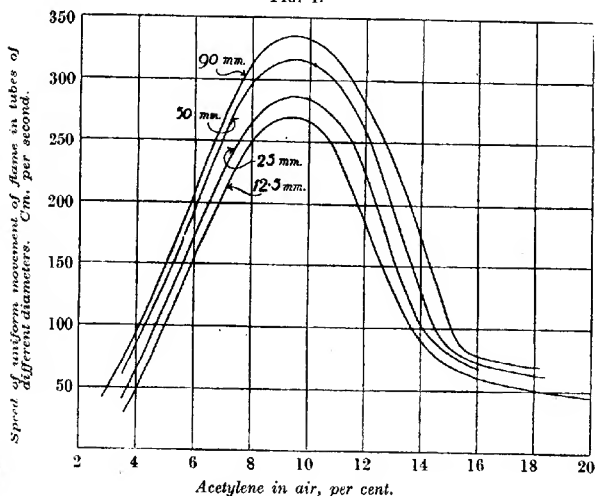
In the present instance, the necessity of avoiding the development of the detonation wave, with consequent shattering of the glass apparatus, demanded that tubes of not much greater length than 150 cm. should be employed. With such short tubes, the uniform movement may give place to the vibratory movement at a distance of less than 20 cm. from the point of ignition (the open end of the tube). It is difficult to record accurately the times of fusion, by rapidly moving flames, of screen-wires placed so close together as this.

There is little doubt but that the inadvertent inclusion of part of the vibratory movement of the flame in the measurement of the speed of the uniform movement has been responsible for some of the discrepant results reported by different experimenters. It would seem most probable that herein lies the explanation of the high velocities recorded by Le Chatelier for the uniform movement of flame in mixtures of acetylene and air in a tube of 40 mm. diameter; for whilst the photographic method of recording the speeds confirms the results obtained by Haward and Sastry when using a tube 12 mm. in diameter, neither in a 50 mm. nor even in a 90 mm. tube did the flames attain during the uniform movement such high speeds as in Le Chatelier's experiments. The maximum speed of flame shown by the photographs during the uniform

movement was 335 cm. per second, for mixtures containing between 9 and 10 per cent. of acetylene (tube 90 mm. in diameter); as compared with 600 cm. per second recorded by Le Chatelier for like mixtures (tube 40 mm. in diameter).

In Fig. 1 the results obtained in the four tubes of different diameters are plotted as speed-percentage curves. The influence of the diameter of the tube on the speed of the uniform movement of flame in mixtures of acetylene and air is shown by this diagram to be of the same degree as with other inflammable gases. For example, the maximum speeds may be compared with those for

FIG. 1.



mixtures of methane and air in tubes of the same diameters (T., 1917, 111, 1052), as follows:

Speed of uniform movement of flame.
Cm. per sec.

| Diameter of tube in mm. | Speed of uniform movement of flame. Cm. per sec. | | Ratio. |
|----------------------------|---|--|--------|
| | Methane-Air (9.5 per cent. CH_4) | Acetylene-Air (9.5 per cent. C_2H_2) | |
| 25 | 67 | 285 | 4.2 |
| 50 | 93 | 315 | 3.4 |
| 90 | 105 | 335 | 3.2 |

The mixture at the lower limit of inflammability, horizontal propagation of flame, contains 2.7 per cent. of acetylene. The upper limit is indeterminate, exothermic decomposition of excess

of acetylene, with deposition of carbon, taking place after a percentage of acetylene of about 17 is exceeded. The speed at which flame travels in the latter mixtures is slow, but does not decrease much with increased acetylene content, as is shown in Fig. 1. According to Le Chatelier, propagation of flame can be obtained (in a tube 40 mm. in diameter) with mixtures containing up to 64 per cent. of acetylene, the speed at the limit being about 5 cm. per second.

Figs. 2-6 reproduce some characteristic appearances of the flames. Each tube was partly covered with black paper, leaving a horizontal slit 5 mm. broad and 30 cm. long, which was focussed on the revolving film. A strip of paper 1 cm. broad divided the slit into two portions, each 14.5 cm. long; this strip appears as a black central line on the photographs. The slit began 10 cm. from the open end, where ignition was effected.

In each instance the flame should be pictured as travelling horizontally from left to right over a measured distance, while the film is moving vertically at a known speed. A curve is thus traced, each point on which has for abscissa the distance travelled by the flame and for ordinate the time that has elapsed since its first appearance at the slit.

Fig. 2. C_2H_2 , 5.40 per cent.—A mixture of the same composition inflamed in tubes of 12.5, 25, and 50 mm. internal diameter and photographed on the same film, the peripheral speed of the drum to which it was attached being 57.6 cm. per second in each instance. The increase of speed of flame with increased diameter of tube is well illustrated by this photograph, and is at once apparent from the angles of inclination of the images. The speeds are: 12.5 mm. tube (A), 120 cm. per sec.; 25 mm. tube (B), 140 cm. per sec.; 50 mm. tube (C), 160 cm. per sec.

Fig. 3. C_2H_2 , 15.00 per cent.—A mixture of the same composition inflamed in tubes of 12.5, 25, and 50 mm. internal diameter. The speed of the film in each instance was 96 cm. per second. It will be seen that with each of the tubes of larger diameter the uniform movement gave place to the vibratory movement after the flame had traversed half the length of the slit, a distance of about 25 cm. from the open end of the tube. The increase in the mean speed of the flame when this transition takes place is well marked.* Only the left-hand halves of the curves

* It is necessary here to note that a distinction must be drawn between the vibrations of large amplitude, accompanied by enhanced mean speed of flame, and the undulations, which are without effect on the speed of the flame, apparent during the "uniform movement" in the larger tubes. The cause of these undulations is explained later.

FIG. 2

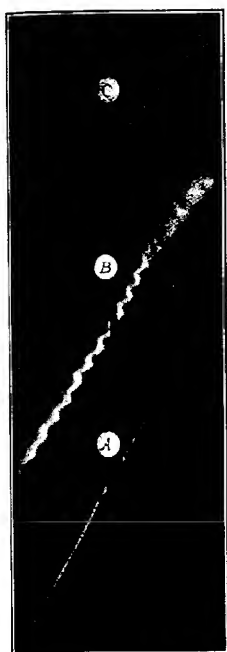


FIG. 3.



[To face page 602.]

Fig. 4.

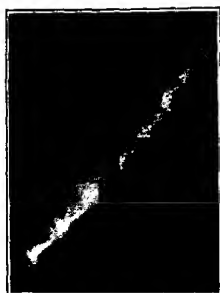


FIG. 5.



FIG. 6.

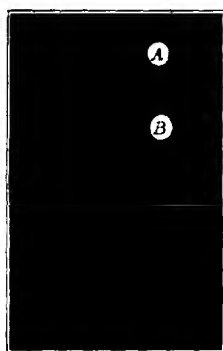


FIG. 7.

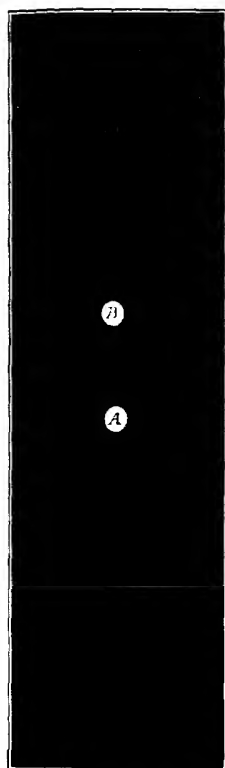
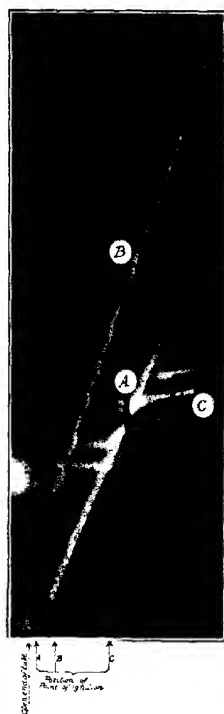


FIG. 8.



can be used for calculating the speeds of the uniform movement, which are: 12.5 mm. tube (*A*), 70 cm. per sec.; 25 mm. tube (*B*), 78 cm. per sec.; 50 mm. tube (unlettered), 85 cm. per sec.

Fig. 4.—Flame travelling in a tube 90 mm. in diameter, the mixture containing 9.45 per cent. of acetylene. Speed of film, 96 cm. per sec. The speed of the uniform movement of this flame (335 cm. per sec.) is the fastest recorded for any mixture of acetylene and air during the course of this research.

Fig. 5.—Flame travelling in a mixture containing 15.55 per cent. of acetylene photographed in a tube of 25 mm. internal diameter. Speed of film, 96 cm. per sec. This mixture contains a considerable excess of acetylene above that required for complete combustion of the oxygen. Secondary combustion took place, air being drawn in from the open end of the tube, whilst the initial flame was travelling a distance of 27–28 cm.; the vibratory movement, with enhanced mean speed of the flame, was then developed.

A feature, common to all the photographs of the flames in the tubes of larger diameter, is the undulating character of the flame front during the uniform movement. The undulations are due to resonance induced in the tubes at the moment of ignition, in part by the compression wave or pulse produced when the suddenly ignited gases expand, and in part by the pulse or train of pulses arising from the source of ignition itself. This, in the majority of the experiments, was a series of secondary discharges across a 3 mm. gap 3 cm. from the open end of each tube, obtained from a "6-inch" induction coil with a current of 10 amperes in the primary circuit. A single such discharge produces a pulse of considerable intensity (see, for example, Töpler, *Ann. Phys. Chem.*, 1867, [ii], 131, 33; 1868, 134, 194), and it is clear from Fig. 6 that the series of discharges used to cause ignition of the mixtures was largely operative in producing the more pronounced undulations of the flame, during the uniform movement.

For this photograph (Fig. 6), a mixture containing 5.4 per cent. of acetylene was ignited in a tube 25 mm. in diameter (*A*) by means of a small hydrogen flame held at the mouth of the tube, and (*B*) by the secondary discharge at the spark-gap 3 cm. within. Both photographs were taken on the same film (speed 55 cm. per second), and the images were good enough to fall close together, so that comparison between them is facilitated. It will be seen that *A* exhibits but slight signs of an undulatory motion of the flame during the uniform movement, whilst in *B* the undulations are well defined and similar in general character to those appearing in the majority of the photographs. The mean speed of the

flame (141 cm. per second) is not affected by the undulations.

No rigid uniformity in the manner of ignition of the mixtures was attempted when determining the speeds recorded in Fig. 1; for, provided that the flame is allowed to travel a sufficient distance before measurement of the speed of the uniform movement is made, the initial impetus given to the flame by the spark dies away. A tapping key was employed, the trembler of the induction coil being allowed to function in the usual manner, and no doubt the discharge was maintained during a longer period in some instances than in others. Experiment showed that prolonged passage of the discharge after ignition had been effected sometimes resulted in the appearance in the photographs of the flames of small undulations superposed on the main undulations, but did not otherwise affect their character.

There remain to be considered the faint undulations apparent in Fig. 6, *A*. These are evidently due to resonance set up in the column of gases in the tubes by the slight shock imparted to it at the moment of ignition, for if great care be taken to avoid any disturbance at the mouth of the tube when igniting the gases, no undulations of the flame appear. In Fig. 7 are reproduced the photographs of flames travelling in a mixture containing 5.15 per cent. of acetylene. For (*A*) ignition was by a small jet of burning hydrogen introduced through a hole 4 cm. from the open end of the tube, whilst for (*B*) a large, flat flame of hydrogen, which more than covered the cross-section of the tube, was used, and this was held momentarily across the mouth of the tube in such a manner that ignition of the mixture took place there simultaneously over the whole surface. With the small source of ignition at a point 4 cm. within the tube, an undulatory motion is imparted to the flame of a more pronounced character than when a similar small source of ignition is held at the mouth of the tube (Fig. 6, *A*). With the large source of ignition (*B*), the propagation of flame is initially absolutely uniform. The speed of the film for these photographs was 96 cm. per second.

Fig. 8 shows the effect of varying the intensity of the compression wave or pulse produced on ignition by varying the volume of mixture contained between the point of ignition and the open end of the tube. The photographs record the progress of the flame from the point of ignition, which was 1 cm. within the tube for (*A*), 4.5 cm. within for (*B*), and 12 cm. within for (*C*). A mixture containing 5.8 per cent. of acetylene was used, and the tube was 25 mm. in diameter. The speed of the film was 100 cm. per

second. Ignition was by a single discharge across a 3 mm. gap produced by breaking a current of 6.6 amperes in the primary of a "10-inch" X-ray coil, the trembler of which was locked.

The "uniform movement" of the flame lies towards the right-hand side of each photograph, that direction of travel being towards the closed end of the tube. Towards the open end the flames travel rapidly, and some of the mixture is projected into the air and burns there. It is clear that the larger the volume of the mixture thus rapidly ignited, and the more intense in consequence the compression wave produced, the greater is the amplitude of the undulations produced in the uniform movement of the flame. When the point of ignition is 12 cm. within the tube, the motion of the flame cannot be regarded as "uniform" at all. (In this connexion, see T., 1917, 111, 1055.)

It may be remarked that the undulatory motion of the flames, even when accentuated by the use of a powerful secondary discharge to ignite the mixtures, is not apparent from direct observation. Its occurrence is rendered evident, however, not only by photographic means, but sometimes also by the appearance along the glass tubes of rings of moisture deposited at regular intervals after the flames have passed. Neyreneuf (*Compt. rend.*, 1880, 91, 321) appears to have obtained similar effects in short tubes coated on the inside with paraffin wax.

The proof that these undulations are indeed resonance effects lies in the close correspondence between their frequencies as determined from the photographs and as calculated from the dimensions of the tubes. Each tube being closed at one end and open at the other, the mode of vibration of the column of gases to give the fundamental tone results, according to Bernoulli's theorem, in an approximate frequency $n = u/4l$, u being the velocity of sound in the gases and l the length of the tube. This approximation assumes a loop, with no pressure variation, at the open end of the tube, a condition which does not obtain. An "end correction" must be applied, which with flanged pipes amounts to about $0.82 r$, and with unflanged pipes to about $0.60 r$ (see Rayleigh, "The Theory of Sound," Vol. 2, p. 183. London, 1896). That is to say, the length of the tube must be increased by $0.82 r$ if flanged and by $0.60 r$ if unflanged before Bernoulli's theorem is applied.

Of the tubes used in the experiments, that of 50 mm. diameter alone was flanged. The observed frequencies of the undulations during the uniform movement of the flames, the dimensions of the tubes, and the calculated frequencies for the fundamental tone

during the longitudinal vibration of air in cylindrical pipes of those dimensions, are given in the table that follows:

| Frequency of undulations during uniform movement of flame. | Dimensions of tube | | Calculated frequency of fundamental tone of tube. |
|--|--------------------|---------------|--|
| | Length. | Diameter. | |
| 63 | 130 cm. | 1.25 cm. | 63.5 |
| 59 | 141 | 2.5 | 58.4 |
| 65 | 126 | 5.0 (flanged) | 64.8 |
| 58 | 140 | 9.0 | 58.1 |

The value taken for the velocity of sound when calculating the frequencies of the fundamental tones of the tubes was 332 m. per second, the velocity in open air at 15°. The velocity in the mixtures in the tubes would vary slightly with the composition of the mixture and the diameter of the tube, but not to a sufficient extent to affect seriously the calculated frequency.

EXPERIMENTAL.

The only part of the experimental arrangements requiring further description is the camera. This consisted of a light-tight box furnished with a lens of quartz 13 cm. in diameter, and containing a drum for the reception of the film, which could be revolved at a high speed.

The focal length of the lens was 17 cm., and its position was fixed once and for all in relation to (1) the tube to be photographed, and (2) the film, so that the size of the image obtained was nearly one-quarter that of the object, the distance of the film from the lens being 20.5 cm.

The drum was 47 cm. in circumference and 10 cm. wide. Its spindle projected at either end through the sides of the camera, and carried at the one end a pulley to receive the drive of an electric motor and at the other end a reduction gearing. This gearing communicated with another drum, of the same diameter as that within the camera, used to receive, on a smoked paper chart, the record of a tuning-fork. The speeds of revolution of the two drums were as 1:32.

All the records of speeds obtained by the photographic method are given in the table that follows. As a check on the method, a series of determinations was made in the 12 mm. tube, using the "screen-wire" method as employed by Haward and Sastry; these determinations are placed within brackets in the table.

| | | Speed of uniform movement of flame. | | | |
|--|-----------|-------------------------------------|-----|----|-----|
| Diameter of tube in mm. = Acetylene in air. Per cent. | | 12.5 | 25 | 50 | 90 |
| 2.75 | — | — | — | — | 40 |
| 3.30 | (26) | — | — | — | — |
| 3.45 | 25 | 41 | 60 | — | — |
| 3.55 | — | — | — | — | 69 |
| 4.00 | (55) | — | — | — | — |
| 4.40 | — | — | — | — | 115 |
| 4.60 | 82 | 95 | 115 | — | — |
| 5.30 | (120) | — | — | — | — |
| 5.40 | 120 | 140 | 160 | — | — |
| 5.80 | — | — | — | — | 195 |
| 6.00 | (155) | — | — | — | — |
| 6.10 | 158 | 172 | 205 | — | — |
| 7.00 | — | — | — | — | 265 |
| 7.05 | 205 | 225 | 250 | — | — |
| 7.15 | (205) | — | — | — | — |
| 7.40 | 220 | 240 | 270 | — | — |
| 7.95 | — | — | — | — | 310 |
| 8.00 | (252) | — | — | — | — |
| 8.15 | 258 | 270 | 303 | — | — |
| 8.60 | (260) | — | — | — | — |
| 8.90 | 265 | 282 | 312 | — | — |
| 9.00 | (268) | — | — | — | — |
| 9.45 | (265) | — | — | — | 335 |
| 9.90 | 266 | 280 | 310 | — | — |
| 10.35 | 260 (265) | 278 | 304 | — | — |
| 10.55 | — | — | — | — | 320 |
| 10.65 | (255) | — | — | — | — |
| 11.00 | (235) | — | — | — | — |
| 11.60 | 206 (210) | 245 | 283 | — | — |
| 11.85 | — | — | — | — | 285 |
| 12.30 | — | — | — | — | 260 |
| 12.40 | (160) | — | — | — | — |
| 12.50 | 150 | 191 | 230 | — | — |
| 13.25 | 115 | 145 | 175 | — | 220 |
| 13.30 | (115) | — | — | — | — |
| 14.00 | 90 | 100 | 115 | — | — |
| 15.10 | 70 | 78 | 85 | — | — |
| 15.30 | — | — | — | — | 84 |
| 15.60 | (65) | — | — | — | — |
| 16.00 | 60 | 68 | 72 | — | — |
| 18.20 | — | — | 60 | 70 | — |

The acetylene was obtained compressed in cylinders, without acetone as solvent, and was of a high degree of purity. The air mixtures were made in metal gas-holders over brine, and were analysed before use.

FSKMEALS,
CUMBERLAND.

[Received, May 8th, 1919.]

XLVIII.—*The Preparation of Diacetoneamine.*

By ARTHUR ERNEST EVEREST.

THE methods for the preparation of diacetoneamine which are described in the literature are laborious and by no means satisfactory, and this applies whether the preparation is through mesityl oxide or by the direct action of ammonia on acetone.

Having need of considerable quantities of the compound, as the starting point for synthetic work, the author tried to find a method which would be both simple in action and satisfactory in respect of yield. The process described below, which was the result of the work, is successful in both respects, and furthermore eliminates almost completely the laborious recovery of mixtures of alcohol and acetone which are formed in the usual process of preparation from acetone and ammonia (see the table below). It enables considerable quantities of diacetoneamine to be prepared with ease and comparative rapidity, and thereby makes this product much more available as a starting point for synthetic work.

One of the chief difficulties in the production of diacetoneamine from acetone and ammonia is the comparatively small amount of ammonia which acetone will dissolve, a fact that necessitates several slow re-saturations being resorted to at intervals of five to seven days. Even when this course is adopted, a large proportion of the acetone remains unchanged. The author has made use of anhydrous calcium chloride to obviate this difficulty. By this means, the whole of the ammonia required can be passed into the reaction mixture in quite a short time, and, moreover, not only does the calcium chloride store up the requisite ammonia, but the water formed as the reaction proceeds is taken up by it, whereby a concentrated solution is formed which separates as a distinct layer and can be removed when the reaction is completed.

EXPERIMENTAL.

Acetone (1160 grams) and anhydrous calcium chloride (200 grams) were introduced into a vessel fitted with a reflux condenser (to prevent loss of acetone during the introduction of ammonia) and an inlet for ammonia. The vessel was then placed in cold water and ammonia (from a cylinder) blown into the mixture as rapidly as the liquid would absorb it (100 grams of ammonia were introduced in quite a short time without any appreciable loss).

Much heat was developed during the addition of the ammonia, but with an effective condenser no loss resulted from this. The introduction of ammonia was continued until the amount absorbed was equal to the weight of the calcium chloride used (200 grams). If it was found that the liquid became nearly saturated before the requisite amount of ammonia had been added (this was rarely the case), the addition of ammonia was stopped, the vessel allowed to remain some eight to ten hours (say overnight), and a further amount of ammonia then added. Before the whole of the ammonia had been introduced, water had usually commenced to separate, a fact that had no detrimental effect on the result.

When 200 grams of ammonia had been blown in, the vessel was allowed to remain at the ordinary temperature for eight to nine days. It was found to be advantageous to shake well once a day during this period. As the reaction proceeded, the compound of calcium chloride and ammonia decomposed, and the products dissolved in the water formed by the reaction, the calcium chloride solution thus produced forming the lower layer in the vessel. Towards the end of the reaction, the upper layer became quite viscous and developed a pale yellow colour, whilst the odour of the amine became noticeable alongside that of ammonia.

When the reaction was completed, the layers were separated, care being taken that all the calcium chloride was removed, as when this was not done, considerable trouble was caused in the filtrations later by the calcium oxalate formed in working up the product. The aqueous layer when extracted with ether yielded a small additional quantity of amine, but in general it was not considered profitable to carry out this operation, and the yields stated below do not include such extractions.

After separation, the amine layer (top) was placed in a vessel and dry air drawn rapidly through it for several hours, whereby a large proportion of the excess of ammonia was removed. The liquid thus obtained possessed a strong odour of the amine. The amount of oxalic acid required for the formation of the hydrogen oxalate was determined (by titration with standard oxalic acid), this was dissolved in alcohol, three times the volume of the reaction mixture being used, and the amine then poured slowly into the alcoholic solution, the whole being kept well agitated. Rectified spirit (B.P.) gave with this process as good results as absolute alcohol had given with other processes, this being due to the fact that the water produced in the reaction was removed, whilst in the older methods it remained in the reaction mixture.

When all the amine had been added, the product, without filtration, was placed in a distilling flask and distilled up to 75°, during

which process a small amount of a mixture of acetone and alcohol passed over (from 1160 grams of acetone, only about 45 grams remained unacted on and passed over in this mixture). At 75°, the distillation was discontinued, and the contents of the distilling flask were rapidly filtered hot. The filtrate, on cooling, deposited diacetoneamine hydrogen oxalate in crystalline condition, which was collected, washed with alcohol, and dried. The solid residue from the hot filtration yielded a small additional quantity of the product when extracted with fresh hot alcohol. From the total mother liquors, a considerable further quantity of pure product was obtained by distilling them on a water-bath until nothing further passed over, allowing the residue to remain for about twenty-four hours in the cold, collecting the crystals which separated, and washing them with alcohol. A certain amount of syrup remained as a by-product, and in this a small amount of triacetoneamine was detected.

By the above method, 800 grams of diacetoneamine hydrogen oxalate (m. p. 125—127°), containing about 1 per cent. of ammonium hydrogen oxalate (see note at end of paper), could be regularly obtained. Of this yield, about 600 grams were obtained from the first deposition and about 200 grams from the liquors and by extraction of the solid residues.

The following table gives comparative results as obtained with the method described above (a), and by the direct action of ammonia on acetone without the use of calcium chloride (b):

| | (a.) | (b.) |
|---|-----------------------------------|------------------------------|
| Acetone taken | 1045 grams | 2100 grams |
| „ recovered | 45 „ | 1100 „ |
| „ used | 1000 „ | 1000 „ |
| Acetone-alcohol mixture fractionated to recover acetone and alcohol ... | 100 c.c. | 2250 c.c. |
| Alcohol used | 3 litres (rectified spirit, B.P.) | 2½ litres (absolute). |
| „ recovered | All; somewhat diluted. | All; considerably diluted. |
| Oxalic acid used | 1050 grams. | 1060 grams. |
| Time of keeping | 8½—10 days. | 24—28 days. |
| Number of saturations with ammonia | One. | 4, at intervals of 5—7 days. |
| Ammonia used (anhydrous) | 190 grams. | 210 grams. |
| Yield | 724 „ | 434 „ |
| By-product: ammonium hydrogen oxalate | 340 „ | 440 „ |

The work described above was carried out in the chemical laboratories of University College, Reading, in February, 1916, and the author desires to thank the Sectional Chemical Committee

of the Royal Society, at whose request the preparation of the diacetanamine was undertaken, for permission to publish the results.

APPENDIX.

Note on Diacetanamine Hydrogen Oxalate and Vinylacetanamine Oxalate.

By ARTHUR ERNEST EVEREST and HAROLD ROGERSON.

In connexion with the work on the new process for the preparation of diacetanamine described above, it was desirable that a ready means of checking the purity of samples of diacetanamine hydrogen oxalate and of vinylacetanamine oxalate should be available. It was further necessary to prove the identity of the products obtained.

In view of the fact that no melting points have been recorded in the literature for these substances, previous workers have at times resorted to the expedient of converting either of the above compounds into a salt of vinylacetanalkamine, liberating the free base, and determining the melting point of this. The fact that this method is obviously unsatisfactory, and that time did not permit of ultimate analysis, led one of us (A. E. E.) to test pure specimens of the above compounds for melting point. It was found that both could be identified by this means. At the same time, the other (H. R.), who was also preparing quantities of these compounds, had quite independently observed that they had sharp melting points. The determinations were therefore mutually confirmed by exchange of specimens.

EXPERIMENTAL.

(a) *Diacetanamine Hydrogen Oxalate.*

A pure specimen of diacetanamine hydrogen oxalate melts fairly sharply at 126–127° to a clear, colourless liquid which, on cooling, sets to a mass of crystals, which again melt at 126–127°. The presence of ammonium hydrogen oxalate in the product causes opalescence in the liquid that results on melting, but has little effect on the melting point. Thus:

Pure diacetanamine hydrogen oxalate melts to a clear liquid at 126–127°.

Pure diacetanamine hydrogen oxalate + 1 per cent. of ammonium hydrogen oxalate melts at 125·5–127°.

Pure diacetanamine hydrogen oxalate + 5 per cent. of ammonium hydrogen oxalate softens then melts at $124.5-126^{\circ}$.

Pure diacetanamine hydrogen oxalate + 10 per cent. of ammonium hydrogen oxalate softens more noticeably then melts at $124-125.5^{\circ}$.

If much ammonium hydrogen oxalate is present in the sample, no melting point is observed, only a softening taking place. This may account for the fact that no melting point has been recorded previously.

A rough approximation of the amount of ammonium hydrogen oxalate in a sample of diacetanamine hydrogen oxalate may be obtained by observation of the degree of opalescence shown when it melts, but for more accurate determinations an extraction of the diacetanamine salt from the sample by boiling absolute alcohol and weighing of the residue is recommended.

(b) *Vinyldiacetanamine Oxalate.*

When this compound is prepared from diacetanamine hydrogen oxalate which contains ammonium hydrogen oxalate, the latter passes through into the product. The presence of ammonium hydrogen oxalate has the same effect on the melting point of vinyldiacetanamine oxalate as it has on that of the diacetanamine salt. If sufficient of the ammonium salt is present, no melting point can be observed, mere shrinkage and change of colour taking place.

Pure vinyldiacetanamine oxalate, prepared from pure diacetanamine hydrogen oxalate and freed from the latter and from oxalic acid by twice boiling with a fairly large quantity of absolute alcohol, filtering hot, and finally washing with boiling absolute alcohol and drying in a vacuum over concentrated sulphuric acid, melts sharply at $184-185^{\circ}$ with the evolution of gas and development of a yellow colour. The presence of diacetanamine hydrogen oxalate in the vinyl compound affects the melting point of the latter considerably and makes it less sharp.

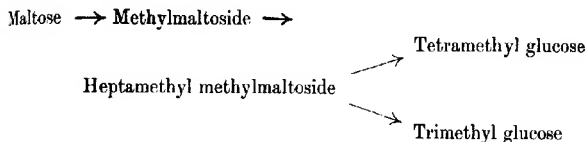
These observations were made at University College, Reading, and at Guy's Hospital Medical School, in February, 1916.

[Received, April 16th, 1919.]

XLIX.—*The Constitution of Maltose. A New Example of Degradation in the Sugar Group.*

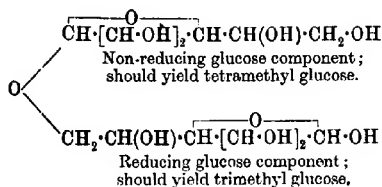
By JAMES COLQUHOUN IRVINE and JAMES SCOTT DICK.

IN the following paper are described the principal results obtained in an investigation undertaken some years ago with the object of determining the constitution of maltose. The standard process was adopted of complete methylation of the disaccharide, followed by identification of the two alkylated sugars produced on hydrolysis, and the series of reactions as originally planned may be represented by the following synopsis:

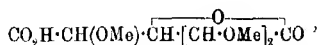


Although the above scheme has not been fully realised, it has been possible to confirm and supplement the earlier results of Purdie and Irvine (T., 1905, **87**, 1022), who showed that the non-reducing glucose component of maltose possesses the butylene-oxide structure, and thus yields crystalline tetramethyl glucose as one product of the above reactions.

This result establishes the constitution of one half of the disaccharide molecule, but, owing to an unexpected degradation of maltose encountered in the course of the work, we have been unable to isolate the trimethyl glucose which should be formed as a second hydrolysis product from a fully methylated maltoside. On the basis of the accepted constitution of maltose, the operation of the series of reactions should give, in addition to tetramethyl glucose, the butylene-oxide form of trimethyl glucose described by Purdie and Bridgett (T., 1903, **83**, 1037). This is shown below:



The identification of the particular form of trimethyl glucose to be expected is, however, difficult in view of the failure of this sugar to give crystalline derivatives, and accordingly, as a necessary preliminary to the present research, we re-examined the compound and determined its physical constants as standards of comparison. In addition, the constitution provisionally assigned to the sugar has been confirmed by a study of its decomposition products. When oxidised drastically by means of nitric acid, the essential product proved to be the monolactone of trimethyl-saccharic acid,



a result which confirms the view that the primary alcohol group in the parent sugar is unsubstituted.

The data thus accumulated proved, however, of little service in the present research, which developed an unexpected but interesting complexity. In preparing the necessary methylmaltoside, we adopted the method described by Mills (*Chem. News*, 1912, 106, 165), in which hepta-acetyliodomaltose is converted into the corresponding acetylated methylmaltoside and the acyl groups are removed by hydrolysis. In the light of subsequent events, this proved to be an unfortunate decision. The various reactions appeared to proceed normally, but, on applying the silver oxide process to the "β-methylmaltoside," we obtained, after three methylations followed by vacuum distillation, a colourless syrup which gave on analysis by Zeisel's method figures agreeing closely with those required for a *hexamethyl methylmaltoside*. In the belief that the methylation was incomplete, further treatments with the alkylating mixture were carried out, but this had no effect on the composition. As a second preparation gave precisely the same result, although the silver oxide reaction was repeated five times, and this was followed by two further methylations, one by means of methyl sulphate and the other by diazomethane, we were forced reluctantly to the conclusion that steric hindrance had interfered completely with the methylation of one hydroxyl group of the maltose molecule.

The results of combustions were indecisive, and the correct interpretation was forthcoming only when the supposed hexamethyl methylmaltoside was hydrolysed, and the two sugars thus produced were separated by distillation in the high vacuum of the Gaede pump. As already mentioned, crystalline tetramethyl glucose was readily obtained as the fraction of lower boiling point, but the remaining product distilled only with the greatest difficulty under

a pressure of 0.1 mm., and could not be induced to crystallise. Examination showed this viscous syrup to be a reducing sugar and to possess the composition of a *dimethyl pentose*, so that clear evidence was thus obtained that, at some stage of the successive reactions, degradation of the maltose molecule had taken place to give derivatives of a sugar containing eleven carbon atoms in the chain. Owing to the close coincidence in the calculated compositions of a highly methylated methylmaltoside and a hexamethyl methylglucopentoside, it was impossible to detect this degradation before hydrolysis, and, owing to the unexpected nature of the result, it was necessary to obtain confirmatory evidence. The dimethyl pentose was therefore converted successively into the corresponding dimethyl methylpentoside and trimethyl methylpentoside, and each compound gave on analysis figures which agree closely with the above explanation. Further, the values found for the specific rotations of these compounds agree with the idea that they are derivatives of arabinose, and the corresponding nomenclature is accordingly employed in the experimental part.

There is little doubt that the degradation took place during the decomposition of maltose octa-acetate by means of hydrogen iodide, and is due to a species of reduction which is unusual in the sugar group. No doubt such a reaction, when once commenced, would be progressive, but in the twelve experiments conducted by us, the change was approximately arrested at a stage when the main product consisted of a derivative of a C_{11} sugar. The maltose originally used was of high purity, and the octa-acetate prepared from it also conformed to accepted standards. On the other hand, the supposed "hepta-acetyl methylmaltoside," obtained after reaction with hydrogen iodide followed by treatment with methyl alcohol, was abnormal. Although apparently a definite chemical individual, we were unable by any process of crystallisation to raise the melting point above $115-117^{\circ}$, whereas the recorded values are higher (Fischer and Armstrong, $121-122^{\circ}$, $125-126^{\circ}$; Königs and Knorr, $128-129^{\circ}$). Fischer has, however, remarked on the difficulty in obtaining this compound pure, and as the method of preparation adopted by us might lead to the production of non-separable α - and β -forms showing a lower melting point, there was no reason at the time to doubt the nature of the compound.

The interruption of our collaboration, due to the War, has prevented us from studying the degradation of sugars by means of hydrogen iodide on more general lines, but the subject is evidently important, as the possibility is opened out of degrading maltose in an acid system and comparing the results with those already

obtained by regulated oxidation in alkaline solution (Lewis and Buckborough, *J. Amer. Chem. Soc.*, 1914, **36**, 2385).

Meanwhile, in a separate research, the results of which will be communicated at an early date, the complete structure of maltose has been established by a method free from the complications now described.

EXPERIMENTAL.

Preparation of Maltose Octa-acetate.

As the preparation of this compound in a pure condition presents considerable difficulty, an account may be given of the method which in our experience proved the most satisfactory.

Pure maltose was acetylated by means of acetic anhydride and sodium acetate in the manner described by Herzfeld (*Annalen*, 1883, **220**, 200), but the reaction was continued for thirty minutes, after which the hot syrup was poured into cold water. On stirring vigorously, the product solidified, and the disintegrated solid was collected, dissolved in alcohol, and the solution neutralised with barium carbonate. The filtered solution was then poured into water, and the solid acetate which separated was collected on a filter and thereafter dried in a vacuum. On extracting the dry crystals repeatedly with a large excess of boiling ether, the impurities remained undissolved, and on removal of the solvents from the united extracts, the acetate was obtained in good yield. One recrystallisation from hot alcohol was then sufficient to give the pure compound melting at 157°.

Action of Hydrogen Iodide on Maltose Octa-acetate.

Sixty grams of the acetate, in portions of 5 grams, were treated in methylene chloride solution with carefully purified hydrogen iodide, as described by Mills (*loc. cit.*). The excess of the gas and the solvent were removed in a high vacuum, and the residual syrup was at once dissolved in dry methyl alcohol, and the solution shaken with silver carbonate until free from iodine. On concentration of the filtrate, the product crystallised readily, but even after repeated crystallisation the melting point could not be raised above 117°.

The yields obtained in the twelve preparations varied considerably, and were in no case more than 60 per cent. of the theoretical amount. Apparently an important factor is to minimise the time during which the acetate is in contact with hydrogen iodide to less than thirty minutes, and to remove the excess of the gas as rapidly

as possible. Otherwise the amount of syrup formed is increased and the proportion of crystalline product seriously diminished.

The removal of the acetyl groups from the supposed hepta-acetyl methylmaltoside was effected in the usual way by shaking with aqueous barium hydroxide, the ultimate product being a glucosidic syrup, which proved to be methylglucoarabinoside. Throughout all the above reactions, the customary precautions were taken to prevent molecular rupture, and the operations were thus extremely tedious.

Methylation of Methylglucoarabinoside.

No details of this reaction need be given, as it was conducted precisely as described in earlier papers dealing with the methylation of glucosides by means of silver oxide and methyl iodide. After two alkylations in methyl-alcoholic solution, the product was freely soluble in methyl iodide, and consequently no extraneous solvent was required in the final methylations. The product, which was a clear, viscid syrup, was purified by fractionation in a high vacuum, and the following table shows that successive treatments did not increase the methoxyl content above a fixed maximum.

| Number of methylations. | B. p. | n_D | Methoxyl. |
|-------------------------|-------------------|--------|-------------------------|
| 4 | 188—190°/0.35 mm. | 1.4692 | 50.34 per cent. |
| 5 | 195°/0.1 mm. | 1.4688 | 50.66 |
| 5 | 205—208°/0.4 mm. | 1.4695 | 52.2, 50.79 " per cent. |
| 6 | 200—203°/0.4 mm. | 1.4689 | 50.45 " |

In a second preparation, otherwise duplicate, the treatment was extended by one methylation by means of methyl sulphate and sodium hydroxide, and finally by diazomethane in ethereal solution, but without alteration in the analytical figures or physical constants of the product. The mean of several consistent analyses gave:

C=52.11; H=8.21; OMe=50.9 per cent.

Heptamethyl methylmaltoside:

$C_{20}H_{38}O_{11}$ requires C=52.86; H=8.37; OMe=54.63 per cent.

Hexamethyl methylmaltoside:

$C_{19}H_{36}O_{11}$ requires C=51.81; H=8.18; OMe=49.3 per cent.

Hexamethyl methylglucoarabinoside:

$C_{13}H_{24}O_{10}$ requires C=52.68; H=8.29; OMe=52.9 per cent.

The results fail to discriminate between the alternatives, and the molecular weight, determined in benzene solution by the cryoscopic method, was equally inconclusive.

Found: 425.

$C_{19}H_{36}O_{11}$ requires 440; $C_{18}H_{34}O_{10}$ requires 410.

On the evidence yielded by hydrolysis, the compound was finally shown to be essentially hexamethyl methylglucoarabinoside ($C_{18}H_{34}O_{10}$).

The new glucoside is a viscid, colourless syrup freely soluble in organic solvents generally, but less so in water. Presumably the specimen examined would consist of both α - and β -forms, so that the specific rotations have only a qualitative significance, but, as is usually the case with methylated compounds possessing the glucose configuration, the activity was but little affected by the nature of the solvent.

| Solvent. | c. | $[\alpha]_D^{20}$. |
|----------------------|-------|---------------------|
| Water | 4.875 | +78.8° |
| Methyl alcohol | 5.609 | 77.5 |
| Ethyl alcohol | 5.316 | 75.9 |
| Acetone | 5.103 | 76.9 |

Hydrolysis of Hexamethyl Methylglucoarabinoside.

Preliminary experiments showed that the double hydrolytic change of removing the glucosidic methyl group and liberating the two constituent aldoses was best effected by boiling a 5 per cent. solution of the above compound in 5 per cent. aqueous hydrochloric acid. This method was accordingly applied to 38 grams of the glucoside, boiling under reflux being continued until the rotation diminished to a constant value, which it did in thirty minutes. The acid was neutralised with barium carbonate, the filtered solution evaporated to dryness under diminished pressure, and the residue extracted with boiling alcohol. After removal of the alcohol, the residual syrup was dissolved in hot acetone, the solution being again filtered and evaporated. The mixed sugars produced in the hydrolysis were obtained in this way as a pale yellow syrup, and were separated by fractionation at the Gaede pump.

A definite first fraction, amounting to 40 per cent. of the total weight, was collected at $125^{\circ}/0.5$ mm. as a moderately mobile liquid, but the remainder of the material distilled only with the greatest difficulty, and presented the appearance of a glass. As much decomposition took place in the later stages of the distillation, no attempt was made, after the first preliminary trial, to distil this product, heating being continued only until the first fraction had been removed.

The more volatile sugar crystallised readily, and, after draining on porous porcelain and two recrystallisations from light petroleum,

was identified as butylene-oxidic tetramethyl glucose melting at 85—87°. (Found: C=50.62; H=8.41; OMe=52.46. $C_{10}H_{20}O_6$ requires C=50.85; H=8.47; OMe=52.54 per cent.)

Mutarotation in alcohol: Initial $[\alpha]_D^{20} + 104.9^\circ \rightarrow$ Final 83.9°.

Identification of Dimethyl Arabinose.—The less volatile sugar solidified on cooling to a glass, and no crystallising medium could be found for the compound, as it is very readily soluble in water or organic solvents, with the exception of light petroleum. It reduces Fehling's solution readily, and is thus a reducing sugar, but gave only syrupy products when treated with aniline, hydroxylamine, or with phenylhydrazine and acetic acid. In approximately 5 per cent. solution, the compound was dextrorotatory:

| Solvent. | $[\alpha]_D^{20}$. |
|--------------------|---------------------|
| Water | +57.7° |
| Ethyl alcohol..... | 56.6 |
| Acetone | 56.9 |

Before determining the activity or the analytical composition, the compound was further purified from traces of tetramethyl glucose by solution in dry ether and the addition of light petroleum, after which the syrupy precipitate was dried in a high vacuum.

The mean of three consistent analyses showed that the sugar was neither the di- nor the tri-methyl glucose expected.

Found: C=47.63; H=7.99; OMe=35.28.

Dimethyl arabinose:

$C_7H_{14}O_5$ requires C=47.19; H=7.86; OMe=34.83 per cent.

Dimethyl glucose:

$C_8H_{16}O_6$ requires C=46.13; H=7.73; OMe=29.8 per cent.

Trimethyl glucose:

$C_9H_{18}O_6$ requires C=48.63; H=8.15; OMe=41.9 per cent.

All the results, and more particularly the methoxyl content, point to the idea that the sugar is a dimethyl arabinose, but further identification was obtained by converting the compound into the corresponding methylpentoside by Fischer's method.

Dimethyl methylaraboside proved to be a colourless syrup (b. p. 120°/0.1 mm., n_D^{20} 1.4620) devoid of action on Fehling's solution until hydrolysed.

Found: C=50.38; H=8.60; OMe=48.9.

$C_8H_{16}O_5$ requires C=50.00; H=8.33; OMe=48.5 per cent.

Further confirmation of the composition of the parent sugar was obtained by subjecting the above pentoside to the silver oxide reaction, so as to produce trimethyl methylaraboside, which was

isolated as a colourless, mobile liquid (b. p. 94–96°/0.08 mm., n_D 1.4460).

Found: C=52.18; H=8.80; OMe=60.1, 60.8.

$C_9H_{18}O_5$ requires C=52.42; H=8.73; OMe=60.2 per cent.

The whole series of analytical results thus consistently supports the view that all the compounds examined are derivatives of a pentose, and not of a hexose. Considering their method of formation, they would consist of mixtures of α - and β -forms, and consequently specific rotations need not be quoted, but the fact that in each case the compounds are strongly dextrorotatory justifies the opinion that they are derived from arabinose, and this is embodied in the nomenclature used.

Trimethyl α -Methylglucoside and Trimethyl Glucose.

The above compounds are already known, but were re-examined for reasons stated in the introduction. Both substances are viscous syrups and yield no crystalline derivatives, so that their identification rests chiefly on the determination of their specific rotations. Unfortunately, the values found by different observers show considerable variation, a fact which may be explained by the difficulty encountered in fractionating syrups of high boiling point under the vacua given by an ordinary water pump, and accordingly we conducted our final distillations under the highly diminished pressure of the Gaede pump.

Fifty grams of α -methylglucoside were dissolved in methyl alcohol and methylated by means of silver oxide (150 grams) and methyl iodide (183 grams), exactly as described by Purdie and Bridgett (*loc. cit.*). After two alkylations, the product was isolated in the usual way and subjected to systematic fractionation, as a result of which 29.5 grams of pure material were obtained after six distillations. The syrup boiled at 160–161°/10 mm., showed n_D 1.4606, and gave $[\alpha]_D^{20} +134.6^\circ$ in absolute alcohol, a value which is not far removed from the specific rotation quoted by Purdie and Irvine (T., 1903, 83, 1021).

On hydrolysis with aqueous hydrochloric acid, the glucoside was converted into trimethyl glucose, the sugar being isolated in the customary manner, and purified by repeated distillations which were continued after satisfactory analytical figures were obtained. The final boiling point recorded was 152–155°/0.02 mm., but the refractive indices and specific rotations shown by the product of different preparations fluctuated widely, although the parent glucoside employed was apparently identical. The

extent of this variation is shown in the two extreme cases quoted below.

In the first preparation, the trimethyl methylglucoside used showed n_D 1.4606 and $[\alpha]_D^{20} + 134.6^\circ$ in methyl alcohol, whilst in the second the corresponding values were 1.4596 and 132.4 . The trimethyl glucose obtained from these two sources showed:

| | Preparation I. | Preparation II. |
|--------------------------------------|----------------|-----------------|
| n_D | 1.4780 | 1.4768 |
| $[\alpha]_D^{20}$ in water | +48.6° | +80.7° |
| $[\alpha]_D$ in methyl alcohol | 48.3 | 65.3 |
| $[\alpha]_D$ in acetone | 46.2 | 58.8 |

In view of these results, there can be little doubt that the sugar and the glucoside from which it was prepared were mixtures of isomerides, and the identification of $\beta\gamma\epsilon$ -trimethyl glucose must in the meantime depend on oxidation processes.

Oxidation of Trimethyl Glucose.

3.5 Grams of the sugar were dissolved in 50 c.c. of nitric acid (D 1.7), and the solution was heated to 80° in order to start the oxidation. Thereafter, the mixture was kept at 65° for three hours, then diluted with water, and evaporated to a syrup under diminished pressure. The process of dilution with water and subsequent evaporation was repeated four times, and was followed by three similar treatments, in which alcohol was used as the diluent. As the syrupy product darkened rapidly at 120° , no attempt was made to distil the compound, which was prepared for analysis by heating at $60^\circ/0.3$ mm. until constant in weight. Analysis showed the substance to be the monolactone of trimethylsaccharic acid.

Found: C=46.07; H=6.33; OMe=37.2.

$C_6H_{14}O_7$ requires C=46.13; H=6.02; OMe=39.7 per cent.

When dissolved in alcohol and rapidly titrated with $N/10$ -sodium hydroxide, the first neutralisation corresponded with the presence of one carboxyl group, and thereafter the compound behaved as a typical lactone on further titration. The lactonic structure was confirmed by the fact that in absolute alcohol the specific rotation remained practically constant, but diminished to a permanent value when aqueous alcohol was used as solvent.

| Solvent. | Initial $[\alpha]_D^{20}$. | Final $[\alpha]_D$. |
|----------------------------|-----------------------------|-----------------------|
| Absolute alcohol | +41.5° | → +43.0° in 48 hours. |
| 50 per cent. alcohol | 43.2 | → 24.0 " " |

We desire to express our indebtedness to the Carnegie Trust for a Research Scholarship which enabled one of us to take part in the work, and also to Miss E. S. Steele, who completed the research when our collaboration was interrupted.

CHEMICAL RESEARCH LABORATORY,
UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD,
UNIVERSITY OF ST. ANDREWS. [Received, May 3rd, 1919.]

L.—Catalytic Racemisation of Ethyl *l*-Mandelate.

By ALEX. MCKENZIE and HENRY WREN.

THE work described in the present communication was suggested by the following observations which have been recorded in the literature dealing with the phenomenon of racemisation.

(1) When an optically active ester is hydrolysed by alkali, it has frequently been found that the product is partly racemised; for example, the specific rotatory power of the barium salt obtained by the action of aqueous barium hydroxide on ethyl *l*-phenyl-ethoxyacetate was only about one-half that of the optically pure salt (McKenzie, T., 1899, 75, 759). Occasionally, the racemisation is even complete; thus, when *l*-mandelic acid was alkylated by a mixture of *n*-propyl iodide and silver oxide, the phenylpropoxyacetic acid isolated from the resulting ester was, contrary to expectation, optically inactive, a result which may now be attributed, in part at least, to the action of the alcoholic alkali employed for the hydrolysis of the ester.* Another example is afforded by the more recent observation of Rupe and Kerkovius (*Ber.*, 1912, 45, 1398), who obtained optically inactive $\alpha\beta$ -diphenylpropionic acid as a consequence of the action of alcoholic alkali on *l*-menthyl *l*- $\alpha\beta$ -diphenylpropionate. Moreover, McKenzie and Miss Widdows showed that the acid isolated from the product of the action of a very slight excess of dilute alcoholic potassium hydroxide on ethyl *d*-phenyl-*p*-tolylacetate was quite inactive.

(2) The gradual racemisation of *l*-mandelic acid when heated

* References on the partial racemisation occurring during the action of alcoholic alkali on optically active esters are the following: McKenzie, T., 1904, 85, 378, 1249; McKenzie and Thompson, T., 1905, 87, 1004, T., 1907, 91, 789; McKenzie and Müller, T., 1907, 91, 1814; McKenzie and Humphries, T., 1909, 95, 1105; McKenzie and Widdows, T., 1915, 107, 702; Wren and Still, T., 1915, 107, 1449; Wren and Williams, T., 1916, 109, 573; Wren, T., 1918, 113, 210.

with alkali was first observed by Holleman (*Rec. trav. chim.*, 1898, 17, 323), whose observations were extended by McKenzie (T., 1904, 85, 385) and by McKenzie and Thompson (T., 1905, 87, 1020). The contrast between the action of aqueous- and ethyl-alcoholic alkali on an optically active acid was studied by McKenzie and Bate (T., 1915, 107, 1681) in the case of *l*-phenylanilinoacetic acid; the effect of the ethyl-alcoholic sodium hydroxide as compared with that of the aqueous alkali was very pronounced, the recovered acids having the values $[\alpha]_D -4^\circ$ and -109° respectively, whilst the pure acid used had $[\alpha]_D -117.9^\circ$ in acetone.

(3) The contrast between the behaviour of *l*-menthyl *l*-mandelate towards aqueous- and ethyl-alcoholic alkali, respectively, as examined by one of us (T., 1904, 85, 1256) is highly significant. The mandelic acid recovered when the hydrolysis was carried out at 100° with the calculated quantity of aqueous alkali gave the value $[\alpha]_D -126.4^\circ$ in aqueous solution, whereas with the calculated quantity of alcoholic potassium hydroxide at 25° the recovered acid had a much lower value, namely, $[\alpha]_D -36.3^\circ$. It was clear from these results, and also from others (for example, in the case of phenyl-*p*-tolylacetic acid), that there is more liability for racemisation occurring during the hydrolysis of esters by alcoholic alkali than by the action of alkali of the free acid. The important inference may be drawn that the active agent in promoting racemisation during the hydrolysis of an optically active ester by alcoholic alkali is the alkoxide rather than the hydroxide.

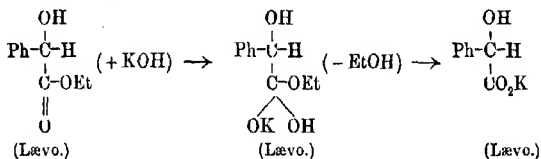
(4) In the course of their examination of the action of alkali on the diastereoisomeric *l*-menthyl phenyl-*p*-tolylacetates, McKenzie and Miss Widdows have pointed out that, when the ester of the *d*-acid was boiled for more than an hour with a slight excess of alcoholic potassium hydroxide, the hydrolysis was incomplete. The ester recovered from this action had, however, the value $[\alpha]_D -54.7^\circ$ in acetone, whereas the pure ester with which the experiment was conducted had $[\alpha]_D -53^\circ$. Small as is the difference between these values, the conclusion that the original ester had undergone partial racemisation was justified. Here the racemisation causes an elevation of the optical rotatory power, inasmuch as the menthyl group in the ester is optically stable towards alkali. This observation is, so far as we are aware, the first example recorded of the catalytic racemisation of an optically active ester by alcoholic alkali. The partial conversion of *l*-menthyl *l*-diphenylsuccinate into *l*-menthyl *meso*diphenylsuccinate, as observed by Wren and Still, has also a bearing on the same problem.

Extending the observations of Wren and Still (T., 1917, 111, 1019) on the formation of ethyl *meso*diphenylsuccinate during the

acid, and the conclusion was reached that the ester was catalytically racemised. The specific rotatory power of the pure ester used was, as already stated, $[\alpha]_D -200.2^\circ$ in carbon disulphide solution. In four separate experiments conducted with alcoholic alkali under different conditions, the ester which had escaped hydrolysis and was recovered gave the values $[\alpha]_D -122.1^\circ$, -105.7° , -91.5° , and -79.5° respectively. Moreover, the effect was more noticeable at higher than at lower temperatures, and it was more extensive in alcoholic than in aqueous solutions; curiously enough, it was more marked with dilute than with concentrated alkali (see table III). The latter observation is interesting and worthy of further investigation; a satisfactory interpretation would doubtless be arrived at by a comparison of the velocity of hydrolysis with the velocity of racemisation in alcoholic solutions of varying concentrations.

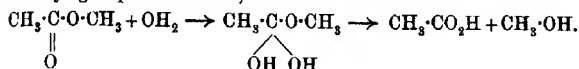
Finally, ethyl *l*-mandelate was hydrolysed by a moderate excess of alcoholic alkali, and the optical rotatory power of the non-hydrolysed ester and of the mandelic acid obtained from the potassium salt was examined at different stages of the hydrolysis. The recovered ester gave the values $[\alpha]_D -162.8^\circ$, -120.2° , and -69.6° respectively in carbon disulphide. As we anticipated, the first portions of the ester to be hydrolysed gave a highly active acid, and the activity of the non-hydrolysed ester always lagged behind that of the acid formed (see table V).

The fact is accordingly established that the action of aqueous alkali on ethyl *l*-mandelate under the conditions quoted in the experimental part is accompanied with very slight racemisation, whereas with alcoholic alkali under similar conditions the racemisation is pronounced. The mechanism of these two actions must obviously be different, and we suggest that with aqueous alkali the following stages may occur:



If the additive compound depicted is formed as an intermediate phase, its existence is presumably only transient, the velocity of its formation being measurably slow as compared with the velocity of its decomposition, which we would suppose to be immeasurably fast. There does not appear to be anything in such an assumption which is opposed either to the bimolecular nature of ester-hydro-

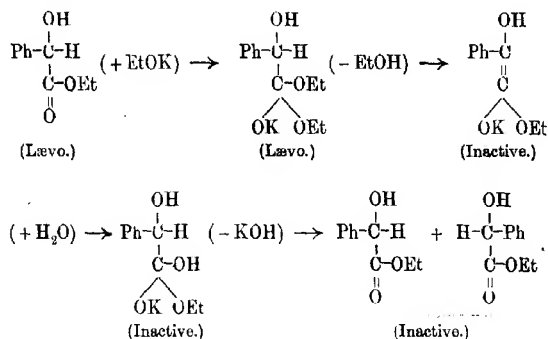
lysis or to the view held by some chemists that ionisation is the final effect instead of the initial cause of chemical reactions, and that association may precede ionisation even in aqueous solutions. A simple interpretation of this kind is not novel, recalling as it does the views advanced, for example, by H. E. Armstrong and Watson (*Proc. Roy. Soc.*, 1907, [A], 79, 579) with reference to the hydrolysis of methyl acetate by hydrochloric acid and nitric acid in the presence of certain salts. Whilst it is admitted by these authors that the hydrated acid is the effective hydrolyst, the assumption is made that water acts alone and attaches itself to the carbonyl group of the ester, thus:



On the basis of their results on the retarding effects of the inorganic salts on the velocity of hydrolysis, the same authors go so far as to assume that the salts actually enter into association with the ester, and consequently hinder to some extent the association of ester and hydrolyst.

Now, on the representation suggested above, ethyl alcohol separates from the additive compound in such a manner that the asymmetry of the molecule is still preserved, the elimination being effected from groups which are not directly attached to the asymmetric carbon atom. If the change proceeded entirely according to this scheme, the mandelic acid resulting from the potassium salt should be the pure levorotatory enantiomorph. In practice, however, the product is always racemised, although only slightly, and this is to be attributed mainly to the presence of a trace of potassium ethoxide formed from the alcohol eliminated. Although the equilibrated condition, $\text{KOH} + \text{C}_2\text{H}_5\cdot\text{OH} \rightleftharpoons \text{KO}\cdot\text{C}_2\text{H}_5 + \text{H}_2\text{O}$, does not appear to have received the attention which its importance deserves, it is nevertheless certain that the quantity of ethoxide present during the hydrolysis of ethyl *l*-mandelate by aqueous alkali under the conditions examined by us can only be extremely small, sufficient, however, to induce the slight racemisation which is invariably observed. If it were feasible to select experimental conditions, of such an order that the ethyl alcohol would at the moment of its formation be removed from the sphere of action without being acted on by the potassium hydroxide, it should be possible to obtain the pure *l*-mandelic acid quite unracemised as the product of the action of the calculated amount of aqueous alkali on the ester. It has, however, to be recognised that under certain conditions racemisation can occur even when alcohol is absent.

On the other hand, since alcoholic potassium hydroxide contains potassium ethoxide, the more pronounced racemisation effects noted with alcoholic alkali are to be attributed to this factor. Here we suppose that the first phase of the action is an additive one, and that the formation of an unsaturated, unstable complex occurs *after the additive compound has been formed*, thus:



According to this picture, the asymmetry of the molecule is destroyed at the stage where the alcohol is eliminated, the ethoxide accordingly causing complete racemisation. A logical deduction would be that it should be possible to effect the complete racemisation of ethyl *l*-mandelate with potassium ethoxide if the experimental conditions could be so adjusted as to prevent the admission of potassium hydroxide into the system.

Wren's observations (T., 1918, **113**, 215) on the action of aqueous-alcoholic alkali on methyl *d*-phenylsuccinate are in harmony with the above views. With the gradual addition of water to alcoholic alkali, the amount of hydroxide will increase, whilst the amount of alkyloxide will diminish. Wren's results show clearly that the addition of water tends to check racemisation to a remarkable extent.

The fact that, when ethyl *l*-mandelate is hydrolysed by a quantity of alcoholic potassium hydroxide insufficient for complete hydrolysis the residual ester is partly racemised, would accordingly be interpreted in the following fashion. A portion of the pure ester is unattacked, whilst another portion is completely racemised by the potassium ethoxide; the ester which escapes being hydrolysed would, therefore, consist of a mixture of *d*- and *l*-esters containing an excess of the latter.

On the other hand, the following distinct reactions appear to

For the neutralisation of 0.38 gram of acid, 22.6 c.c. of 0.1105*N*-alkali are required. When a slight excess of alkali of this concentration was employed, there was still racemisation; the effect of raising the temperature is, however, clearly indicated, as also is the greater racemising effect of the alcoholic as contrasted with the aqueous alkali. The effects of the more concentrated alkali (0.93*N*) were more pronounced. Although the value -146.6° obtained from the third experiment quoted in the above table is not far removed from that of the optically pure *l*-mandelic acid, the racemisation which occurred when the alcoholic solution was kept at the ordinary temperature and submitted to polarimetric examination at intervals was observed quite clearly, the α_D falling from -1.21° to -1.08° ($l=1$) after seven days. At 70.5° , the initial value for α_D was -2.42° ($l=2$); after one hour α_D was -2.15° , and after three hours -1.92° , whilst the acid recovered after the action had proceeded for thirteen hours had a value so low as $[\alpha]_D -61.2^\circ$. It must, of course, be noted that the alkali in this experiment was present in considerable excess. On the other hand, with aqueous alkali (0.93*N*), the initial value for α_D was -2.89° ($l=2$); after three hours at 70.5° , the value had fallen to -2.80° , and after thirteen hours to -2.45° , whilst the recovered acid had $[\alpha]_D -127.4^\circ$ after the action had been in progress for thirteen hours.

With regard to the conditions, the experiments quoted in the table are strictly comparable, as they were performed simultaneously.

Complete Hydrolysis of Ethyl l-Mandelate by Potassium Hydroxide.

The ester was prepared by esterifying the acid with ethyl alcohol and sulphuric acid. Its rotation was determined in carbon disulphide:

$$l=2, c=2.0155, \alpha_D^{25} = -8.07^\circ, [\alpha]_D^{25} = -200.2^\circ.$$

This value is higher than that quoted by Walden (*Zeitsch. physikal. Chem.*, 1895, 17, 708), who gives $[\alpha]_D -180^\circ$ in carbon disulphide for $c=2.5$.

CATALYTIC RACEMISATION OF ETHYL L-MANDELATE. 611

TABLE II.

| Ester, grams. | Alkali. | Alkali required. | Conditions. | $[\alpha]_D$ of recovered acid. |
|------------------|-----------------------------------|---------------------|------------------------|------------------------------------|
| 0.697 | 35.5 c.c. alcoholic (0.1105N). | 35.0 c.c. | 3 days at ord. temp. | -86.0° ($c=1.9$) |
| 0.697 | 35.5 c.c. alcoholic (0.1105N). | " | 6 hours at 70° | 74.5 ($c=2.32$) |
| 0.789 | 80 c.c. alcoholic (0.1105N). | 39.6 | 5 days at ord. temp. | 93.7 ($c=2.05$) |
| 0.789 | 80 c.c. alcoholic (0.1105N). | " | 6 hours at 70° | 80.6 ($c=2.62$) |
| 1.0639 | 6.6 c.c. alcoholic (0.93N). | 6.35 | 20 hours at ord. temp. | 112.4 ($c=3.16$) |
| 1.0639 | 6.6 c.c. alcoholic (0.93N). | " | 3 hours at 70° | 105.1 ($c=3.07$) |
| 0.721 | 10 c.c. alcoholic (0.93N). | 4.3 | 2 days at ord. temp. | 118.4 ($c=2.05$) |
| 2.0516 | 10 c.c. alcoholic (2.18N). | 5.2 | 1½ hours at ord. temp. | 124.1 ($c=2.14$) |
| 0.5192 | 27 c.c. aqueous (0.1105N). | 26.1 | 4 days at ord. temp. | 149.4 ($c=1.8$) |
| 0.5893 | 30.5 c.c. aqueous (0.1105N). | 29.6 | 6 hours at 70° | 152.2 ($c=1.93$) |
| 0.9408 | 6 c.c. aqueous (0.93N). | 5.6 | 1 day at ord. temp. | 147.3 ($c=2.99$) |
| 0.9008 | 5.8 c.c. aqueous (0.93N). | 5.4 | 4 hours at 70° | 146.5 ($c=3.24$) |
| 0.6785 | 8.1 c.c. aqueous (0.93N). | 4.0 | 2½ hours at 70° | 144.8 ($c=2.06$) |

Experiments with excess of hot concentrated alcoholic alkali were not performed, since the product would have been appreciably racemised by the alkali after the completion of the hydrolysis, and the value for the specific rotation would have varied according to the duration of heating.

Our thanks are due to Mr. Henry Wood, who in 1906 carried out the following experiments with the methyl and propyl esters of *l*-mandelic acid. A mixture of 3 grams of methyl *l*-mandelate and 50 c.c. of an aqueous solution of potassium hydroxide (1.114 grams, calculated 1.014 grams) was maintained at the ordinary temperature for seven days. The acid obtained gave the value $[\alpha]_D -153.9^\circ$ for $c=1.99$. An experiment conducted under similar conditions with 3 grams of the ester and 48.5 c.c. of alcoholic potassium hydroxide (1.016 grams) gave an acid with $[\alpha]_D -115.9^\circ$. These results showed the difference between the behaviour of aqueous and alcoholic alkali. When propyl-*l*-mandelate was hydrolysed with a slight excess of aqueous alkali at the ordinary temperature, the acid recovered gave the value $[\alpha]_D -149.4^\circ$; the behaviour of this ester towards alcoholic alkali was not examined at the time.

Partial Hydrolysis of Ethyl l-Mandelate.

(1) *With Ethyl-alcoholic Potassium Hydroxide (0.1105N).*—Ester, 3.7273 grams; 94 c.c. of alkali (calculated 187.3 c.c.). The solution was divided into two equal parts: (a) *At the ordinary temperature for forty-eight hours.*—The alcohol was removed from the neutral solution by evaporation, the residue added to water, and the non-hydrolysed ester extracted with ether and dried; its rotation determined in carbon disulphide solution was $[\alpha]_D -105.7^\circ$ for $c=2.19$. The mandelic acid was obtained from the potassium salt in the usual manner, and its rotation determined in aqueous solution was $[\alpha]_D -119.9^\circ$ for $c=3.03$. (b) *At 70° for four hours.*—Recovered ester, $[\alpha]_D -79.5^\circ$ for $c=4.69$; acid, $[\alpha]_D -110.9^\circ$ for $c=3.57$.

(2) *With Ethyl-alcoholic Potassium Hydroxide (0.93N).*—Ester, 3.4658 grams; 10 c.c. of alkali (calculated 20.7 c.c.). The solution was divided into two equal parts: (a) *At the ordinary temperature for twenty-four hours.*—Recovered ester, $[\alpha]_D -122.1^\circ$ for $c=3.15$; acid, $[\alpha]_D -131.3^\circ$ for $c=3.37$. (b) *At 70° for six hours.*—Recovered ester, $[\alpha]_D -91.5^\circ$ for $c=2.13$; acid, $[\alpha]_D -122.1^\circ$ for $c=2.31$.

(3) *With Aqueous Potassium Hydroxide (0.93N).*—Ester, 3.4156 grams; 10 c.c. of alkali (calculated 20.4 c.c.). *At the ordinary temperature for three days.*—Recovered ester, $[\alpha]_D -181.8^\circ$ for $c=4.82$; acid, $[\alpha]_D -152.2^\circ$ for $c=2.02$.

These results are contrasted in the following table.

TABLE III.

| Alkali. | t. | Ester hydro-lysed, per cent. | $[\alpha]_D$ of residual ester. | $[\alpha]_D$ of acid. | Race-misation of ester, per cent. | Race-misation of acid, per cent. |
|--------------------|------------|------------------------------|---------------------------------|-----------------------|-----------------------------------|----------------------------------|
| Alcoholic 0.1105N. | Ord. | 50.2 | -105.7° | -119.9° | 47.2 | 22.3 |
| | 70° | " | 79.5 | 110.9 | 60.3 | 28.2 |
| Alcoholic 0.93N | Ord. | 48.3 | 122.1 | 131.3 | 39.0 | 15.0 |
| | 70° | " | 91.5 | 122.1 | 54.3 | 20.9 |
| Aqueous, 0.93N | Ord. | 49.0 | 181.8 | 152.2 | 9.2 | 1.4 |

Examination at Different Stages during the Complete Hydrolysis of Ethyl l-Mandelate by Alcoholic Alkali.

The ethyl-alcoholic potassium hydroxide used was 0.202N. Six grams of the ester were dissolved rapidly at the ordinary temperature by shaking with 205 c.c. of alkali (calculated 165 c.c.). At intervals, 50 c.c. of the solution were withdrawn and run into a

slight excess of standard sulphuric acid, the solution being then titrated with standard alkali. In each case, the alcohol was removed by heating, and the ester and mandelic acid in the residue were separated as usual.

TABLE IV.

| Interval. | Solution withdrawn. | Sulphuric acid, 0.998N. | 0.202N-alkali required for excess of acid. |
|-----------|---------------------|-------------------------|--|
| 7 minutes | 50 c.c. | 10 c.c. | 11.0 c.c. |
| 25 " | " | " | 23.0 " |
| 65 " | " | " | 33.9 " |
| 1269 " | " | " | 40.1 " |

In table V, the specific rotatory power of the mandelic acid was determined in ethyl-alcoholic solution, the acid from which the ethyl *l*-mandelate was prepared having $[\alpha]_D -152^\circ$ for $c=1.671$ in ethyl alcohol.

TABLE V.

| Fraction. | Ester hydrolysed, per cent. | $[\alpha]_D$ of ester recovered. | $[\alpha]_D$ of acid. | Ester racemised, per cent. | Acid racemised, per cent. |
|-----------|-----------------------------|----------------------------------|-----------------------|----------------------------|---------------------------|
| 1 | 28 | $-162.8^\circ (c=2.45)$ | $138.2^\circ (c=1.1)$ | 18.7 | 9.1 |
| 2 | 58 | $120.2 (c=1.46)$ | $119.0 (c=1.02)$ | 40.0 | 21.7 |
| 3 | 84 | $69.6 (c=0.52)$ | $104.3 (c=2.85)$ | 65.2 | 31.4 |
| 4 | 100 | — | $96.3 (c=2.69)$ | — | 36.6 |

UNIVERSITY COLLEGE, DUNDEE,
UNIVERSITY OF ST. ANDREWS,
MUNICIPAL TECHNICAL INSTITUTE,
BELFAST.

[Received, May 8th, 1919.]

II.—The Potential of a Nitrogen Electrode.

By FRANCIS LAWRY USHER and RAMAVENKATASUBBIER
VENKATESWARAN.

THE decomposition potential of a normal solution of hydrazoic acid has been found by Le Blanc to be 1.29 volts, and this acid therefore resembles the halogen acids (except hydrofluoric) in furnishing at the anode an electromotively active substance the potential of which is lower than that of oxygen. The substance in question has been presumed to be ordinary nitrogen, so that it should be possible to construct a nitrogen electrode similar to a chlorine or a hydrogen electrode, and to measure its potential in a solution containing N'_3 ions. An attempt which we have made to do this

has led to some interesting results, which leave little doubt that the substance set free at the anode in the electrolysis of azide solutions is not ordinary nitrogen, but an active form of it. Some purely chemical evidence in support of this conclusion was obtained by one of us in 1914, and it is proposed to resume these experiments as soon as circumstances permit; they are at present too incomplete for publication.

EXPERIMENTAL.

The *E.M.F.* of the combination $N/10\text{-calomel}|N/100\text{-KCl}|N/100\text{-NaN}_3|N_2Pt$ was measured at 30° , the nitrogen employed being carefully freed from oxygen and oxides. The nitrogen electrode was about 0.4 volt negative to the calomel, and therefore slightly negative to hydrogen, a result which is clearly incompatible with the assumption that the nitrogen furnishes N'_3 ions reversibly. It was, in fact, proved that the observed potential was unaffected by the presence of nitrogen. The attempt was repeated with several different kinds of electrode, but always with the same negative result.

Since the nitrogen liberated at the anode during the electrolysis of azide solutions is electromotively active, as shown by the existence of a definite decomposition voltage, it appeared probable that at the moment of its liberation it was different from, but was very rapidly converted into, ordinary nitrogen. It was therefore decided to polarise a platinum wire anodically in an azide solution with a definite *E.M.F.* in slight excess of the decomposition voltage, and to measure its potential, which would be slightly higher than the true potential corresponding with the reversible change $N'_3 \rightleftharpoons$ active nitrogen. The electrolytic cell was made of paraffined teak-wood divided into three compartments by parchment paper diaphragms, the three compartments containing *N*-sodium azide, with some hydrazoic acid added to the middle compartment in order to neutralise any ammonia formed by reduction at the cathode. The potential of the anode was measured against a *N*/10-calomel electrode at the ordinary temperature ($25\text{--}26^\circ$). The results read from the smoothed curves are shown in the following table. In Series I, about 5 cm. of platinum wire 0.5 mm. thick were used, in Series II about 2 mm. of the same wire, and in Series III a short point of very fine wire. the metal being well platinised in every case.

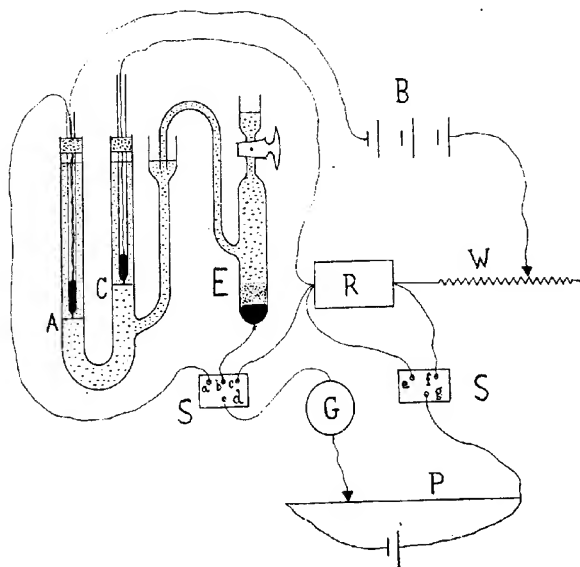
| Applied <i>E.M.F.</i> Volts. | Potential of anode against <i>N/10</i> -calomel. | | |
|---------------------------------|--|-------|-------|
| | I. | II. | III. |
| 1.20 | 0.690 | 0.760 | 0.788 |
| 1.30 | 0.698 | 0.770 | 0.800 |
| 1.40 | 0.704 | 0.782 | 0.813 |
| 1.50 | 0.712 | 0.797 | 0.829 |
| 1.60 | 0.722 | 0.812 | 0.843 |
| 1.70 | 0.732 | 0.830 | 0.861 |
| 1.80 | 0.743 | 0.848 | 0.880 |
| 1.90 | 0.754 | 0.873 | 0.904 |

Although the combination was so arranged that the potentials at the liquid junctions could be calculated after determining the transport number for sodium azide, it was unnecessary to do this, because, as is evident from the above table, a constant value for the potential of the nitrogen electrode was not obtained at any applied voltage. Its behaviour appears to be normal so far as the effect of increasing voltage is concerned, but depends on the size of the anode, that is, on the current density. The current flowing in the primary circuit was at all times sufficient to cause a brisk evolution of gas, so that the results cannot be attributed to want of saturation. With a view to investigate the relation between the potential and the current density, a series of measurements was made with varying but known current densities at a constant decomposing voltage.* The arrangement shown diagrammatically in the accompanying figure was used. The solution of *N*-sodium azide, slightly acidified with hydrazoic acid, was contained in a tall U-tube with a side branch for the calomel electrode (*E*). The electrodes (*AC*) consisted of platinised platinum disks sealed into glass tubes which passed through corks, and could be moved up or down. The U-tube was tilted when in use in order to prevent an accumulation of gas under the disks. The electrolysing current was furnished by a battery (*B*), and passed through an adjustable low resistance (*W*), a resistance box (*R*), and the solution in the U-tube. *SS* are two paraffin block switches of which the terminals *d* and *g* were connected to a potentiometer (*P*), the other connexions being as shown in the diagram. In taking a series of readings, the circuit was first closed, *e* was connected to *g*, and *a* to *d*. Plugs were then taken out of the resistance box until the potential difference across the U-tube was approximately 1.31 volts (chosen as being slightly in excess of the decomposition voltage), and the rheostat (*W*) was then adjusted so that that figure was exactly attained. The second measurement was that of the fall of potential across the resistance box, and the third gave the *E.M.F.* of the combination nitrogen-

* Keys, standard cell, and a buffer solution between the U-tube and calomel electrode are not shown.

calomel. The current flowing through the solution was known from the second measurement, which gave the fall of potential across a known resistance, and from this the current density was calculated, the area of the anode being always the same, namely, 0.65 sq. cm. By altering the position of the electrodes, the resistance of the solution could be varied, and therefore also the current density.

It was noticed that when the platinised electrodes were immersed in the solution, a slow evolution of nitrogen occurred even when no current was passed. This could not have been due to occluded



chlorine derived from the platinising liquid, since it took place after soaking the electrodes in ferrous sulphate solution and washing them thoroughly, but was probably due to catalytic decomposition by the platinum black. Shortly after this observation was made, we found that the phenomenon had already been studied by Oliveri-Mandalà (*Gazzetta*, 1916, **46**, ii, 137). The platinum apparently became "poisoned" after the evolution had proceeded for some time, and nitrogen ceased to be given off after the first series of readings had been taken. The following table shows the results obtained. The current density at the anode (C.D.) is given

ii) microamperes per sq. cm., and the *E.M.F.* of the combination in volts.

| I. | | II. | | III. | | IV. | |
|------|---------------|------|---------------|------|---------------|------|---------------|
| C.D. | <i>E.M.F.</i> | C.D. | <i>E.M.F.</i> | C.D. | <i>E.M.F.</i> | C.D. | <i>E.M.F.</i> |
| 4707 | 0.446 | 4070 | 0.493 | 3659 | 0.508 | 3768 | 0.494 |
| 4838 | 0.468 | 4244 | 0.506 | 3738 | 0.524 | 3816 | 0.518 |
| 4975 | 0.482 | 4285 | 0.516 | 3831 | 0.542 | 3847 | 0.545 |
| 5136 | 0.497 | 4377 | 0.528 | 3893 | 0.558 | 3893 | 0.561 |
| 5444 | 0.520 | 4541 | 0.540 | 4019 | 0.577 | 3988 | 0.587 |
| 5741 | 0.541 | 4670 | 0.552 | 4112 | 0.593 | 4051 | 0.617 |
| 6131 | 0.564 | 4868 | 0.561 | 4237 | 0.608 | 4144 | 0.652 |
| | | 4992 | 0.581 | 4364 | 0.629 | | |
| | | 5157 | 0.590 | | | | |
| | | 5362 | 0.615 | | | | |
| | | 5546 | 0.635 | | | | |

If the above figures are plotted on a curve, it is seen that, as one would expect, the rate of increase of potential with current density diminishes as the latter increases. Since the potential is a measure of the concentration of the electromotively active substance in the electrode (assuming the solution to remain unaltered), it is evident that the latter is unsaturated even when nitrogen is being evolved freely, and one can only explain this behaviour by assuming that the N'_3 ions furnish an active form of nitrogen on discharge, and that this is rapidly converted into ordinary nitrogen, probably catalytically by the platinum.

It has been shown in other instances that the velocity of reaction between a gas and a solid is proportional to the partial pressure of the gas. In the present case, the rate of formation of active nitrogen must be proportional to the current density, and its rate of decomposition may be considered proportional to its partial pressure, that is, to its concentration, of which the potential is a known function. If, therefore, the measurements correspond with a state of equilibrium (which they probably do, since the potential shows no variation so long as the current density remains constant),* we obtain the relation: rate of formation of active nitrogen = $k_1 D$ = rate of decomposition = $k_2 C$, where D is the current density and C the concentration of active nitrogen. If P is the measured *E.M.F.*, we get † $P = a + b \log D$, where a and b are constants. The following table shows the experimental values of the *E.M.F.* in Series II, the values read from a smoothed curve drawn through

* In the four series of readings given, the actual values of the potential in the different series are not the same for a given current density. This variation is due to differences in the solutions, and is not observed in a solution of definite composition.

† By substituting $C = k_1 D / k_2$ in the expression $P = a + b \log c$, and collecting the constant terms.

the figures enclosed in brackets, and the values calculated by means of this expression:

| C.D. | E.M.F. | | |
|--------|-----------|---------------------------|-------------|
| | Measured. | Read from smoothed curve. | Calculated. |
| (4070) | (0.493) | (0.493) | (0.493) |
| 4244 | 0.506 | 0.512 | 0.512 |
| 4285 | 0.516 | 0.516 | 0.516 |
| 4377 | 0.528 | 0.526 | 0.525 |
| 4541 | 0.540 | 0.542 | 0.542 |
| 4670 | 0.552 | 0.554 | 0.554 |
| 4818 | 0.561 | 0.568 | 0.568 |
| 4992 | 0.581 | 0.584 | 0.584 |
| 5157 | 0.590 | 0.598 | 0.598 |
| (5362) | (0.615) | (0.615) | (0.615) |
| 5546 | 0.635 | 0.630 | 0.630 |

The agreement between the observed and calculated figures is satisfactory, and probably indicates that the assumptions made are in the main correct. It is interesting to note that the above expression does not fit the curve obtained in Series I, where the solution was being decomposed catalytically during the observations, but that if a third constant (representing a constant additional supply of active nitrogen) is introduced, the agreement becomes good.

An attempt was made to obtain some idea of the rate at which the active nitrogen is decomposed in contact with the electrode. An azide solution was electrolysed in such a way that the gas accumulated in bubbles under the anode. On breaking the decomposing current, the potential fell at first so rapidly that it could not be followed, and dwindled to zero in about thirty seconds. A similar experiment with chlorine showed that the potential fell by 0.2 volt in twenty minutes, and a hydrogen electrode by 0.06 volt in the same time, so that the result with nitrogen cannot be explained by diffusion.

The only reference to any peculiarity in the chemical properties of the nitrogen obtained by electrolysing an azide appears to be in a paper by Browne and Lundell (*J. Amer. Chem. Soc.*, 1909, **31**, 435), who electrolysed a solution of potassium azide in anhydrous azoimide at -78° , and, on the occasions when their apparatus was not shattered, observed that the gas evolved at the anode attacked mercury. Apparently, therefore, the active nitrogen is much less rapidly decomposed at a low temperature.

CENTRAL COLLEGE,
BANGALORE, S. INDIA.

[Received, March 3rd, 1919.]

LII.—*A Chemical Investigation of Banded Bituminous Coal. Studies in the Composition of Coal.**

By FREDERICK VINCENT TIDESWELL and RICHARD VERNON
WHEELER.

It is, and has been since pit-coal first, became an article of daily use, a matter of common observation that any lump of bituminous coal taken haphazard is almost certain to exhibit, in a more or less marked degree, differences in the texture of its surface which give it a banded appearance, the bands being alternately dull and bright.

The subject of the banded appearance of bituminous coal has recently been treated in a more exact manner than heretofore by Stopes (*Proc. Roy. Soc.*, 1919, [B], 90, 470), whose observations can be briefly summarised as follows.

She distinguishes, not merely "dull" and "bright" bands, but four distinctive portions forming the mass of an ordinary bituminous coal. The four portions can be recognised and separated from each other both macroscopically and microscopically in thin sections. These four ingredients were provisionally named by Stopes:

- (i) Fusain. The equivalent of "mother-of-coal," "mineral-charcoal," etc., of various authors.
- (ii) Durain. The equivalent of "dull" hard coal of various authors; the "Mattkohle" of the Germans.
- (iii) Clarain. } Together the equivalent of "bright" or "glance" coal of
- (iv) Vitrain. } various authors; the "Glanzekohle" of the Germans.

These show various differences in character, and, in particular, markedly distinct microscopical features.

Microscopical and palæobotanical study has thus been able to distinguish between four visible ingredients in banded bituminous coal, and to ascribe to each a character essentially different from the others as regards the appearance and probable nature of the materials of which it is composed. As a corollary to this work, we have undertaken to determine to what extent, or if at all, the four ingredients differ amongst themselves in their chemical nature as ascertained by ordinary methods.

So far as we are aware, the only previous detailed attempt to relate the texture with the chemical composition of a coal is that

* The work by Dr. M. C. Stopes, the reference to which is given below, forms No. 1 of this series of researches.

by Grout (*Econ. Geol.*, 1911, 6, 449), who made a careful study of selected parts of a black lignite or sub-bituminous coal from Gorham Mine, Marshall, Colorado. Several references are to be found, it is true, to the difference in composition between a sample of "mother-of-coal" (fusain) and the coal with which it was associated; and there has been a tendency on the part of some writers to confuse fusain, which may occur in bands or layers, but is just as often present in coal in numerous very small pockets, with "dull" or "matt" coal (durain) (see, for example, Strahan and Pollard, *Mem. Geol. Surv. Engl. Wales*, 1915, 6, 91).

We do not propose to discuss the reason for the gross difference that undoubtedly exists between the chemical composition of fusain and that of coal, but to reserve such a discussion for a future memoir, since it belongs more properly to a disquisition on the mode of formation of the coal conglomerate. Our immediate concern is with the more subtle differences in composition that can be presumed to be correlated with the characteristic appearances of vitrain, clarain, and durain.

The coal chosen for this research was, for obvious reasons, one of those used by Dr. Marie Stopes for her investigations, namely, the Thick Coal, Hamstead Colliery. We are indebted to her for volunteering the task—a laborious one requiring much care—of providing supplies of each macroscopically distinct ingredient, free from the others, sufficient for chemical examination. The total supply was obtained from blocks of coal collected within a few cm. of each other in the same portion of the seam.

The fusain was obtained as a powder by scraping lightly with a knife at such cleavage surfaces as had wedges of the material on them. The durain was obtained as small blocks or broken bands by splitting off from it all bright streaks. To obtain the durain reasonably pure, it was necessary to split the coal considerably; although preponderatingly dull in appearance, a few bright streaks of hair-like fineness remained in it. In contrast to the brittle, powdery fusain, the durain is firm and hard.

Clarain preponderated in the sample. It is throughout banded finely with rather brighter and rather duller portions, but in general it has a subdued surface lustre when viewed broken at right angles to the bedding plane, which is distinct from the matt surface of the durain.

Vitrain is a conspicuous feature in a block of this coal. It was separated as small splints and cubes through the ready breaking up of its layers. The vitrain runs in horizontally extended bands varying from 1 to 6 mm. in thickness. Unlike the clarain, a single band does not show banding within itself, but the face at right

angles to the bedding plane is uniformly and brilliantly glossy, and instead of the usual cleavage the fracture tends to be conchoidal.

The methods of chemical investigation employed for each of the four ingredients have been: proximate and ultimate analysis; the action of solvents and of reagents; and destructive distillation in a vacuum, with examination of the gaseous and liquid products. A tabulation of the results obtained, so far as they admit of tabulation, is given later. Some description is first required of the different operations, further details of which are given in the experimental portion of the paper.

The Action of Solvents.—Extractions were made in Soxhlet fat-extraction apparatus, using from 1 to 10 grams of material ground so as to pass through a 200 × 200 mesh sieve.

(1) *Pyridine:*

| | Vitrain. | Clarain. | Durain. | Fusain. |
|--|-----------|-----------|---------------|---------|
| Extract, per cent. on ash-free, dry coal | 34.4 | 27.2 | 21.6 | 10.1 |
| Colour of solution | Dark red. | Dark red. | Brownish-red. | Brown. |

(2) *Chloroform Extraction of Pyridine Extract.*—One gram of each of the dried extracts of vitrain, clarain, and durain was extracted with chloroform during two days. Extraction appeared to be complete after twelve hours. The percentage of the pyridine extract soluble in chloroform was with vitrain 27, with clarain 30, and with durain 40.

From these results, the percentages of α -, β -, and γ -compounds present in the coal (see Stopes and Wheeler, "Monograph on the Constitution of Coal," 1918) can be calculated as follows:

| | Vitrain. | Clarain. | Durain. |
|---|----------|----------|---------|
| α -Compounds (insoluble in pyridine)... | 65.8 | 72.8 | 78.4 |
| β -Compounds (soluble in pyridine, but insoluble in chloroform) | 25.0 | 19.0 | 13.0 |
| γ -Compounds (soluble in both pyridine and chloroform) | 9.2 | 8.2 | 8.6 |

Samples of vitrain and durain were extracted direct with chloroform and with ethyl alcohol; the percentages extracted are recorded in table V.

The Action of Reagents. (1) *Alcoholic Potassium Hydroxide.*—This reagent has been used by previous workers to determine the quantity of ulmin compounds present in a coal. The substances removed are no doubt ulmin compounds, but all such compounds are not necessarily soluble in aqueous or alcoholic potassium hydroxide (Stopes and Wheeler, *loc. cit.*); it is better, therefore, simply to record the fact that a certain portion of a coal is soluble in the

reagent, without attempting to draw any conclusion therefrom as to the total percentage of ulmin compounds present.

A modification of Hart's method of treatment (*Chem. Zeit.*, 1907, **31**, 640), in which the reagent is maintained at 80°, was used in the first instance, the results being:

| | Vitrain. | Clarain. | Durain. |
|--|----------|----------|---------|
| Soluble in hot alcoholic potassium hydroxide; per cent. on ash-free, dry coal | 6.1 | 5.4 | 3.8 |

Stopes had observed that in the cold this reagent seemed to have a peculiar effect on vitrain, causing small lumps to "acquire the consistency of hard cheese or soap," so that thin flakes could be cut from it with a razor, whilst in untreated coal vitrain is hard and resistant to a cutting edge. It seemed desirable, therefore, to determine whether prolonged treatment of the powdered coals in the cold would result in greater quantities passing into solution. The percentages removed after eight weeks of such treatment were:

| Vitrain. | Clarain. | Durain. |
|----------|----------|---------|
| 5.7 | 5.2 | 3.6 |

The softening or loosening action of the alkali observed by Stopes would thus appear to be caused by the removal of some binding material from the coal conglomerate; the ulmin compounds have been credited with a binding or cementing action.

(2) *Iodine*.—The absorption of iodine by coal may be regarded as giving an approximate measure of the proportion of unsaturated compounds present.

Before treating the four ingredients of banded coal, preliminary trials were made with other coals to determine the conditions of test most likely to yield accurate comparative results. These trials showed that iodine absorption by coal is very slow and may continue for a long time. It was, in fact, found to be impracticable to determine the maximum amount of iodine that can be absorbed by coal, for the absorption varied with the conditions, and more particularly with the length of duration of test. For example, Wijs' solution (iodine chloride in solution in glacial acetic acid), although causing about four times the absorption given by aqueous iodine, yet did not appear to be within measurable distance of giving a final value after twelve hours.

In recording the results that follow, it is necessary to distinguish between "permanent" and "temporary" absorption of iodine (see p. 635). The results given are strictly comparative, each of the four components of banded coal being treated under identical conditions.

TABLE I.

Iodine Absorbed per cent. by Weight on Ash-free, Dry Coal.

| Duration of treatment. Hours. | Temporary. (Released on keeping.) | | | | Permanent. | | | |
|--|--------------------------------------|----------|---------|---------|------------|----------|---------|---------|
| | Vitrain. | Clarain. | Durain. | Fusain. | Vitrain. | Clarain. | Durain. | Fusain. |
| 1. | 6.4 | 7.6 | 4.1 | 0.7 | 8.6 | 6.9 | 6.8 | 2.1 |
| 3. | 7.9 | 8.3 | 5.5 | 0.7 | 14.3 | 11.8 | 12.3 | 3.6 |
| 6. | 9.3 | 9.7 | 6.8 | 1.4 | 16.5 | 16.0 | 13.0 | 2.9 |
| 24. | 10.7 | 10.4 | 8.9 | 2.1 | 22.8 | 23.6 | 17.8 | 4.3 |

These results were obtained with aqueous iodine ($N/10$ in potassium iodide solution). With Wijs' solution, the following quantities of iodine, calculated as percentages on the ash-free, dry coals, were absorbed during six hours:

| Temporary. | | | | Permanent. | | | |
|------------|----------|---------|---------|------------|----------|---------|---------|
| Vitrain. | Clarain. | Durain. | Fusain. | Vitrain. | Clarain. | Durain. | Fusain. |
| 18.6 | 20.8 | 17.1 | 8.6 | 67.9 | 63.2 | 51.3 | 4.3 |

Destructive Distillation. Gaseous Products.—The procedure adopted for the examination of the gaseous products was that of fractional distillation in a vacuum. In this manner, the ranges of temperature over which decompositions occurred, with the production of one or other of the usual constituents of coal-gas in predominant quantity, became manifest. With each of the four ingredients of banded coal, decomposition, as evinced by the evolution of gases in any quantity, did not become marked until a temperature of about 350° was reached, although slight decomposition occurred with each at a temperature of 300° . At 200° , with all except fusain, a trace of gas was evolved, together with a little liquid having an odour of light petroleum.

The tabulated results of the distillations are as follow:

TABLE II.

Vitrain.

| Temperature | 0-300 | 300-350 | 350-400 | 400-450 | 450-500 | 500-550 | 550-600° |
|---|-------|---------|---------|---------|---------|---------|----------|
| Vol. of gas at N.T.P. evolved per gram of coal, c.c. | 5.0 | 6.2 | 22.5 | 25.9 | 37.4 | 49.8 | 52.0 |
| Analysis, per cent. | | | | | | | |
| $C_4H_4 + C_mH_{2m}$ | 8.3 | 12.0 | 8.8 | 2.2 | 0.7 | nil | nil |
| $CO_2 + H_2S$ | 58.3 | 20.4 | 7.3 | 3.3 | 2.3 | 1.1 | 1.1 |
| O_2 | 0.5 | 0.4 | nil | nil | nil | nil | nil |
| C_2H_2 | 1.8 | 4.8 | 4.8 | 1.9 | 0.4 | nil | nil |
| CO | 21.7 | 20.8 | 14.8 | 15.1 | 15.0 | 11.3 | 12.1 |
| H_2 | .. | 2.8 | 9.7 | 35.2 | 59.8 | 80.1 | 82.2 |
| C_2H_4 | 8.0 | 38.8 | 55.1 | 42.3 | 21.8 | 7.5 | 4.6 |
| Ratio C/A on explosion for paraffins | 1.50 | 1.56 | 1.80 | 1.85 | 1.95 | 2.00 | 2.00 |

TABLE II. (continued).

Clarain.

| Temperature..... | 0-300 | 300-350 | 350-400 | 400-450 | 450-500 | 500-550 | 550-600° |
|---|-------|---------|---------|---------|---------|---------|----------|
| Vol. of gas at N.T.P. evolved per gram of coal, c.c. | 4.5 | 5.4 | 19.8 | 23.0 | 35.0 | 35.7 | 50.0 |
| Analysis, per cent. | | | | | | | |
| $C_2H_4 + C_2H_{2n}$.. | 9.0 | 10.0 | 9.0 | 2.3 | 0.9 | nil | nil |
| $CO_2 + H_2S$ | 58.5 | 24.5 | 10.6 | 6.3 | 4.0 | 1.4 | 1.3 |
| O_2 | 0.5 | 0.3 | trace | nil | nil | nil | nil |
| C_2H_4 | 1.5 | 4.2 | 4.6 | 2.0 | 0.3 | nil | nil |
| CO | 21.0 | 21.6 | 14.4 | 14.5 | 14.0 | 11.9 | 12.3 |
| H_2 | — | 3.0 | 9.3 | 33.0 | 58.5 | 76.0 | 80.0 |
| C_nH_{2n+2} | 7.5 | 34.4 | 52.1 | 41.9 | 22.3 | 10.0 | 6.4 |
| Ratio C/A on explosion for paraffins | 1.52 | 1.60 | 1.71 | 1.80 | 1.90 | 2.00 | 2.00 |

Durain.

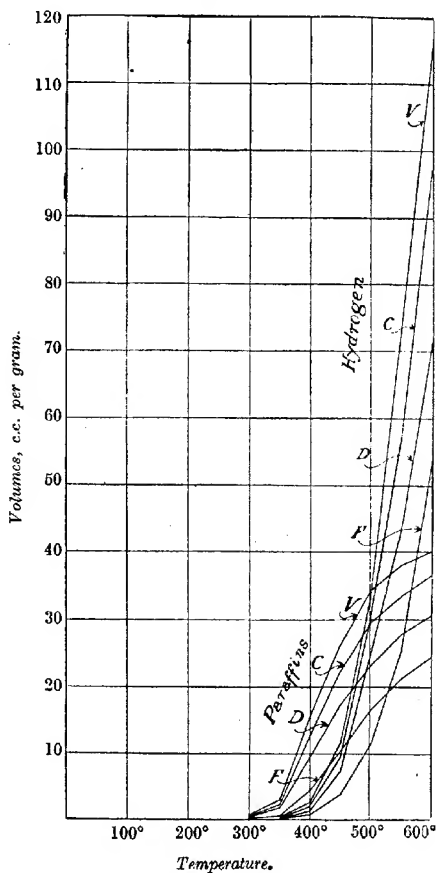
| Temperature..... | 0-300 | 300-350 | 350-400 | 400-450 | 450-500 | 500-550 | 550-600° |
|---|-------|---------|---------|---------|---------|---------|----------|
| Vol. of gas at N.T.P. evolved per gram of coal, c.c. | 3.55 | 5.4 | 15.4 | 18.9 | 31.0 | 30.0 | 35.8 |
| Analysis, per cent. | | | | | | | |
| $C_2H_4 + C_nH_{2n}$ | 11.6 | 14.4 | 11.7 | 2.5 | 1.8 | nil | nil |
| $CO_2 + H_2S$ | 58.7 | 28.3 | 13.8 | 9.2 | 6.7 | 6.2 | 2.0 |
| O_2 | 0.6 | 0.4 | 0.1 | nil | nil | nil | nil |
| C_2H_4 | 1.0 | 3.3 | 4.3 | 2.1 | 0.3 | nil | nil |
| CO | 19.3 | 19.1 | 12.4 | 13.5 | 15.0 | 16.4 | 12.6 |
| H_2 | nil | 3.0 | 7.7 | 32.1 | 56.6 | 62.7 | 77.0 |
| C_nH_{2n+2} | 7.3 | 29.8 | 50.0 | 40.6 | 19.6 | 14.7 | 8.4 |
| Ratio C/A on explosion for paraffins | 1.40 | 1.45 | 1.70 | 1.85 | 1.95 | 2.00 | 2.00 |

Fusain.

| Temperature..... | 0-300 | 300-350 | 350-400 | 400-450 | 450-500 | 500-550 | 550-600° |
|---|-------|---------|---------|---------|---------|---------|----------|
| Vol. of gas at N.T.P. evolved per gram of coal, c.c. | 1.8 | 2.0 | 7.5 | 12.0 | 17.5 | 22.0 | 35.0 |
| Analysis, per cent. | | | | | | | |
| $C_2H_4 + C_nH_{2n}$ | 11.5 | 8.9 | 7.5 | 2.8 | 1.8 | 0.7 | nil |
| $CO_2 + H_2S$ | 56.4 | 38.0 | 20.0 | 11.4 | 8.2 | 6.4 | 3.8 |
| O_2 | nil | nil | nil | nil | nil | nil | nil |
| C_2H_4 | 2.3 | 3.5 | 3.0 | 2.2 | 0.7 | 0.2 | nil |
| CO | 20.8 | 20.1 | 16.0 | 15.8 | 18.1 | 17.2 | 13.3 |
| H_2 | nil | 2.4 | 10.6 | 22.6 | 38.4 | 56.7 | 73.9 |
| C_nH_{2n+2} | 3.0 | 23.0 | 42.3 | 45.2 | 32.8 | 18.5 | 9.0 |
| Ratio C/A on explosion for paraffins | 1.25 | 1.42 | 1.60 | 1.82 | 1.90 | 2.00 | 2.00 |

In Figs. 1 and 2 are shown the volumes of individual gases plotted against the temperatures at which they were evolved. The

FIG. 1.



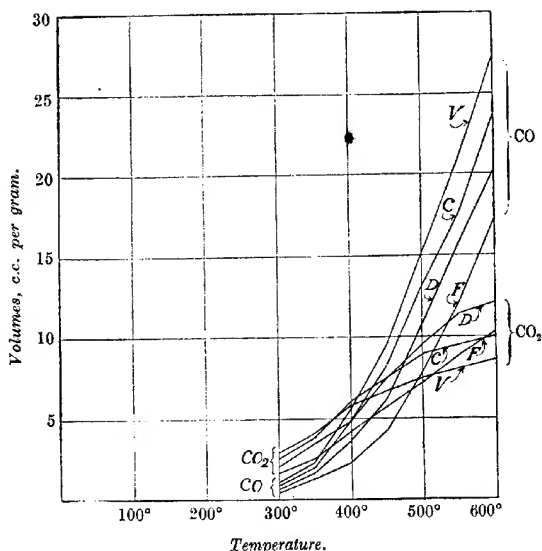
curves thus obtained show clearly the various stages of decomposition of the coal.

Destructive Distillation. Primary Liquid Products.—Only vitrain and durain were submitted to destructive distillation with

a view to examine the primary liquid products. Of fusain, an insufficient quantity was obtainable, whilst it seemed probable that the behaviour of clarain could be deduced from that of the other two components of banded coal, which would, at all events, afford the maximum degree of contrast. The records of the distillations are as follow.

Vitrain. May 31st, 1918.—The apparatus (see p. 636) having been exhausted of air, heating was begun at 2.0 p.m., the temperature being raised slowly to 100°. This temperature was main-

FIG. 2.



tained until noon on June 3rd. Water collected in the cooled receivers. *June 3rd.*—The temperature was raised gradually to 300°. Water and a little gas were evolved as the temperature increased. Oils began to appear at 300°. *June 4th.*—Increase of temperature was continued very slowly from 300° in order to determine the point at which active decomposition began. This was found to lie between 350° and 360°, over which range there was a rapid evolution of gas, water, and oils. Throughout the day the temperature was raised slowly to 400°. Viscid red oils began to appear at 390°, and their quantity increased with increase

temperature up to 455° (June 5th). *June 5th—7th.*—The temperature was raised, in stages of 25°, up to 550°. A rapid evolution of gas occurred at each successive increment of temperature, but there was no further appreciable production of oil or tar above 460°.

Durain. June 14th.—Heating begun, the temperature being raised slowly to 100°, and the water that was driven off collected. The temperature was maintained at 100° overnight. *June 15th—17th.*—Temperature raised to 150°; very little more water was collected. Temperature raised slowly from 150° on the morning of June 17th; at 11.45 a.m., the temperature being 250°, water made a reappearance in quantity in the distillates; at 12.45 p.m., temperature 300°, oils began to collect in the receivers, but the evolution of gases was small. The rate of production of oils increased steadily with increased temperature without a corresponding increase in the quantity of gases; between 350° and 360°, the rate of evolution of gases increases slightly, but there was no marked decomposition point until the range 370—380° was reached. *June 18th—24th.*—The sequence of events as the temperature was raised gradually to 550° was the same as with vitrain, except that a notable evolution of water occurred at 450°. As with vitrain, there was but little production of oil or tar above 480°.

The main products of the distillations, calculated as percentages, by weight, on the ash-free, dry coals, may be tabulated as follows:

TABLE III.

| | Vitrain. | Durain. |
|----------------------------|----------|---------|
| Residue (ash-free) | 79.0 | 79.0 |
| Water of decomposition ... | 6.7 | 5.8 |
| Tar and oils | 5.6 | 8.0 |
| Gas (by difference) | 8.7 | 7.2 |

From the tar and oils there were obtained on distillation:

| | | |
|------------|-----|-----|
| Oils | 3.6 | 4.0 |
|------------|-----|-----|

The oils were composed of:

| | | |
|-------------------|-----|-----|
| Phenols | 2.2 | 1.6 |
| Neutral oils..... | 1.4 | 2.4 |

The residue remaining in the retort in each instance consisted of loose particles little different in appearance from the original materials. With durain there were slight indications of coherence of some of the particles; no coherence could be observed with vitrain. With the latter there was a shrinkage in volume amounting to about 25 per cent. of that of the original coal; with the former, the shrinkage was only about 10 per cent.

Examination of the Liquid Distillates.—Owing to the small quantities obtained, it was not possible to make a complete examination of the fractions collected at different temperatures. Up to 150°, with both vitrain and durain, the distillates consisted of water; both were neutral and colourless and free from oils and organic or mineral salts.

The distillates obtained between 150° and 300° were aqueous, with traces only of hydrocarbon oils. They fumed strongly in air, and were found to be concentrated solutions of hydrochloric acid. There was evidence of the presence of compounds of the polyphenol type in traces.

The aqueous portions separated from the distillates between 300° and 500° were also strongly acid (hydrochloric acid). On adding excess of potassium hydroxide, the vitrain distillate evolved an inflammable gas, strongly alkaline and with an odour like that of methylamine, whilst the durain distillate evolved a strongly alkaline gas, not unlike pyridine in odour. No ammonia could be detected in either distillate. Colour reactions for polyhydric phenols were again noted.

The method of examination of the tar and oils was, for both vitrain and durain, to mix together the fractions obtained at different temperatures and distil them under reduced pressure. The oils obtained were treated with solutions of sodium carbonate and potassium hydroxide to remove phenols, with hydrochloric acid to remove traces of bases, and finally with water. The phenols were liberated from their alkaline solution and distilled, as were the neutral oils. The results are best shown in parallel columns.

TABLE IV.

| Vitrain. | Durain. |
|---|---|
| Below 250° (40 mm.) 64 per cent. of the tar distilled without decomposition. At 250° decomposition began. The oils that passed over at that temperature began to solidify on cooling. | Below 300° (25 mm.) 60 per cent. of the tar distilled without decomposition. Above 260° the oils coming over began to solidify on cooling. At 300° decomposition began with evolution of HCl. |
| | The oils were poured off from the solid distillate. |

Examination of the oils showed:

| | Vitrain. | Durain. |
|--|--------------|--------------|
| Soluble in dilute Na ₂ CO ₃ solution | 10 per cent. | 40 per cent. |
| Soluble in 15 per cent. KOH solution ... | 50 " | |
| Soluble in HCl | traces | traces |
| Neutral oils | 40 per cent. | 60 per cent. |

TABLE IV. (*continued*).

Examination of the phenols showed:

| Vitrain. | Durain. |
|---|---|
| The sodium carbonate solution contained polyphenols (<i>o</i> -dihydroxy). The phenols liberated from the potassium hydroxide solution gave on distillation: | The total phenols on distillation gave: |
| (1) 50 per cent. boiling at 200–212°. | (1) 25 per cent. boiling at 200–220°. |
| (2) 25 per cent. boiling at 260–280°. | (2) 25 per cent. boiling at 240–280°. |
| (3) 25 per cent. residue. | (3) 50 per cent. residue. |
| Fraction (1): C=76.96; H=7.76. D ₁₅ ⁴ 1.025. | Fraction (1): C=78.49; H=8.67. |
| Fraction (2): C=78.12; H=7.70. Very viscous. | Fraction (2): C=80.86; H=7.91. Very viscous. |

Examination of the neutral oils showed:

| Vitrain. | Durain. |
|--|---|
| Distilled almost completely at 160–320°. | Distilled almost completely at 160–340°. |
| C=85.86; H=9.91 (C+H=95.8). | C=85.44; H=10.39 (C+H=95.8). Charring with cold sulphuric acid left only about 10 per cent. of saturated hydrocarbons. |

It will be noticed that the phenols derived from both coals fall into two well-defined groups, the first distilling at 200–220°, the second at 240–280°. The first group, in their constants and analyses, in their colour reactions with ferric chloride and other salts (aqueous and alcoholic), and in their phthalic anhydride condensations, agreed with the lower simple phenols, and were presumably cresols and xylenols. There was evidence also of the presence of some more complex phenol, or phenol ether, perhaps guaiacol. The second group gave pronounced colour reactions of the polyhydric phenols, and more particularly of the *o*-dihydroxy-benzenes, but probably consisted mainly of condensed products. Protocatechuic acid, or a similar compound, was present in the washings from the phenols before their final distillation. This decomposes normally at about 200°, but may easily have escaped decomposition under the conditions of the distillations. Durain gave a more complex mixture of phenols than vitrain.

The distilled neutral oils from both coals were very similar, yellowish-brown oils. They did not consist exclusively of hydrocarbons, and the proportion of saturated hydrocarbons was low.

Paraffin wax was obtained in quantity from the higher boiling fractions of each tar.

The general analytic results can be summarised as follows:

TABLE V.

| | Vitrain. | Clarain. | Durain. | Fusain. |
|--|----------|----------|---------|---------|
| Density | 1.290 | 1.280 | 1.395 | — |
| <i>Ultimate analysis.</i> —Per cent. on ash-free, dry coal: | | | | |
| Carbon | 78.5 | 79.1 | 80.8 | 84.7 |
| Hydrogen | 5.15 | 5.2 | 5.1 | 3.9 |
| Oxygen | 13.9 | 13.4 | 11.8 | 9.7 |
| Nitrogen | 1.33 | 1.28 | 1.3 | 1.05 |
| Sulphur | 1.12 | 1.02 | 1.0 | 0.65 |
| <i>Proximate analysis:</i> | | | | |
| Moisture, per cent. | 12.6 | 10.2 | 6.5 | 3.9 |
| Ash, per cent. | 1.2 | 1.45 | 3.6 | 10.0 |
| Volatile matter, per cent. on ash-free, dry coal | 38.6 | 40.8 | 39.4 | 22.6 |
| <i>Extractions.</i> —Per cent. on ash-free, dry coal: | | | | |
| By pyridine | 34.4 | 27.2 | 21.6 | 10.1 |
| By alcohol | 6.6 | 5.7 | 3.1 | — |
| By chloroform | 2.85 | — | 2.4 | — |
| Pyridine extract soluble in chloroform, per cent. | 27.0 | 30.0 | 40.0 | — |
| Percentages of α -, β -, and γ -compounds in the coal: | | | | |
| α -Compounds | 65.8 | 72.8 | 78.4 | — |
| β - " | 25.0 | 19.0 | 13.0 | — |
| γ - " | 9.2 | 8.2 | 8.6 | — |
| <i>Action of reagents.</i> —Per cent. on ash-free, dry coal: | | | | |
| Solubility in alcoholic potassium hydroxide: | | | | |
| (1) Hot | 6.1 | 5.4 | 3.8 | — |
| (2) Cold | 5.7 | 5.2 | 3.6 | — |
| Iodine absorption (permanent): | | | | |
| N/10-aqueous iodine, in 24 hours | 22.8 | 23.6 | 17.8 | 4.3 |
| Wij's solution, in 6 hours | 67.9 | 63.2 | 51.3 | 4.3 |

The general impression created by an examination of the results recorded in this table is of a gradation of properties as we pass from vitrain to durain. Fusain, as already noted, stands apart in its character from the other three ingredients of banded coal. The ultimate analyses show a steady rise in carbon and fall in oxygen content in the order (1) vitrain, (2) clarain, and (3) durain, and this order is maintained with practically every property investigated.

Thus there is a regular reduction in moisture content and increase in ash content. The marked retention of moisture by vitrain most probably results from its colloidal nature, indicated by the conchoidal fracture and the absence of any recognisable structure. The ash content may to a certain extent affect the surface lustre of the coal. Indeed, from chemical examination alone, one might be tempted to say that durain is durain because it is rich in ash; but it is clear from the work of Stopes that the decisive factor affecting the lustre is the presence or absence of plant structure. No doubt there is a direct connexion between the ash content of a coal and the presence of plant remains therein.

The results of extractions both by organic solvents and by alcoholic potassium hydroxide exhibit well the gradation in properties from vitrain to durain; they also suggest a lack of homogeneity in vitrain not evident from microscopical examination. The fact that both vitrain and durain (and, it may be assumed, clarain also) contain nearly the same proportions of γ -compounds is striking. The chief difference between the ingredients of banded coal, as revealed by the action of pyridine and chloroform, lies, therefore, in the amounts of α - and β -compounds present. If, as has been suggested, the action of pyridine is mainly a mechanical loosening of the structure of the coal conglomerate, the α - and β -compounds may actually be, as from their chemical behaviour they appear to be, essentially similar in character. From this point of view, the main difference between vitrain and durain would be a physical one, and would lie in the ease with which their (colloidal?) structures are disintegrated. The fact that the action of chloroform direct on the coals is to remove much smaller proportions of soluble matter than when an attack is first made with pyridine is in agreement with this suggestion.

Alcohol appears to dissolve a portion of the coal conglomerate unaffected by chloroform—possibly the “resins,” using the word in its strictest sense. It is noteworthy that the proportions dissolved are higher than is usual with bituminous coals.

Perhaps the most striking evidence of gradation in properties of the four ingredients is afforded by the destructive distillations with examination of the gaseous products (see table III and Figs. 1 and 2). The volume-temperature curves obtained for the individual gases run nearly parallel, each to each, there being a rapid evolution of paraffins beginning at 350° and of hydrogen beginning at 400°.

The quantities of each gas (carbon dioxide excepted) evolved over equal temperature ranges are greatest with vitrain and least with fusain, clarain and durain occupying intermediate positions.

The analyses of the gases evolved from each at any given temperature interval are very similar; it is their quantity that differs. The difference between the coals—between vitrain and durain, for example—is therefore not such as exists between α - β - and γ -compounds, which yield distinctive gaseous mixtures on destructive distillation, the former being rich in hydrogen and the latter rich in paraffins (Clark and Wheeler, T., 1913, 103, 1704). The parallel volume-temperature curves show that for each of the four components of banded coal the relative production of hydrogen and paraffins is approximately the same, indicating that each contains similar proportionate amounts of the two characteristic ingredients of coal, namely, α - and β -compounds (regarded together as being similar in their behaviour on destructive distillation) and γ -compounds.

For carbon dioxide, the same order is preserved up to 400°, but is reversed at higher temperatures. With fusain, the evolution of carbon dioxide is constant for each interval of 50° between 350° and 600°.

On comparing the records of the distillations conducted on a larger scale with vitrain and durain, it will be seen that in general durain required higher temperatures to resolve it. Vitrain had a well-defined decomposition point at 350–360°, with a rapid evolution of gas and oil, whilst the decomposition point of durain was less well marked at 370–380°. Moreover, all the tar obtainable from vitrain had distilled over before a temperature of 460° was passed, whereas with durain tar was still produced at 480°.

Vitrain yielded less tar than durain, the same amount of residue, but more water of decomposition and more gas. The tar from vitrain yielded less pitch than that from durain, the quantity of oils finally obtained from the two coals being nearly the same. A difference between the distillates further appears in the character of the oils.

The high proportion of phenols in the tar oils, and the oxygenated character of the neutral oils, which contained but little saturated hydrocarbons, is noteworthy. Jones and Wheeler (T., 1914, 105, 140) found from 12–15 per cent. of phenols in the tar oils from a Durham bituminous coal, and later (T., 1915, 107, 1318) showed that these were produced exclusively from the “cellulosic” (α - and β -compounds) portion of the coal. The large proportion of phenols in the tar oils from the Hamstead coal used in the present research (50 per cent.) is due to the nature of the coal, which is highly oxygenated (10–13 per cent. of oxygen), a fact which also accounts for the oxygenation of the neutral oils.

It is not possible in the present state of ignorance of the chemical

composition of coal to draw precise conclusions regarding any difference in constitution that may exist between vitrain, clarain, and durain. The chemical data obtained point to the differences that might be expected to accompany the obvious difference in physical character being of degree rather than of kind. No characteristic reaction or behaviour for any one of the components of banded coal, such as might be expected were there a fundamental difference in the chemical composition of the coals, was disclosed.

The analytical results indicate for clarain a composition approximately one-third the way between vitrain and durain. It is interesting to find, therefore, that as we pass from vitrain to durain, the "reactivity" of the coal (that is to say, the extent of its susceptibility towards solvents and reagents) diminishes in the ratio vitrain:clarain:durain=1:0.9:0.7. This relationship applies also to the results of destructive distillation (except as regards the proportions of carbon dioxide evolved).

Such a relationship can be explained on the assumption that the coals are composed of a "reactive" group of compounds, together with a relatively "inert" material. The former alone is attacked by solvents, responds to reagents, and yields the main bulk of the gases and tars on distillation. The latter is chiefly responsible for the evolution at the higher temperatures of carbon dioxide on destructive distillation, and perhaps also for the neutral oils. It is clear, also, that the "reactive" group of compounds must contain more oxygen and less carbon than the "inert."

On this assumption, vitrain, clarain, and durain are similar as regards the composition of the "reactive" material they contain, as is shown by the approximate constancy of the ratios of "reactivity," but differ in the proportions of "reactive" and "inert" constituents they contain; it is conceivable, also, that the character of the latter varies, though a consideration of the ultimate and proximate analyses of the three ingredients does not point to this being so.

Summary.

In the banded Hamstead coal investigated, the ingredients (leaving out of account fusain) show differences which grade them in the sequence vitrain, clarain, and durain. This sequence is evidenced in the fall in the moisture- and rise in ash-content; in the increase of carbon- and decrease of oxygen-content; and in the diminishing "reactivity" towards solvents, reagents, and heat treatment.

Whilst making clear interesting differences which would scarcely

have been expected from portions of coal so immediately adjacent in the same seam, the work has not revealed the presence of essentially distinct types of chemical compounds peculiar to any one of the ingredients of banded coal.

That portion of each ingredient responsible for the reactions observed appears to be of nearly constant composition. It is suggested that the difference between the ingredients lies in the proportion of "inert" or unresponsive material with which this "reactive" portion is associated. If a given weight of vitrain be assumed to contain x parts by weight of "reactive" material, the same weight of clarain would contain $0.9x$ and of durain $0.7x$ parts.

Correlation of the microscopical with the chemical and other data available respecting banded bituminous coal is reserved for a future communication.

EXPERIMENTAL.

The various operations were conducted throughout under conditions strictly comparative for the four ingredients of the banded coal.

Analyses.—For the proximate analyses, the methods recommended by the American Chemical Society were employed. The ultimate analyses were made in the usual manner, sulphur being determined by Eschka's and nitrogen by Kjeldahl's method. For the estimation of carbon and hydrogen, the combustion tube was packed with copper oxide and lead chromate. The four ingredients differed considerably in their behaviour during combustion, fusain burning with difficulty in oxygen, whilst the combustion of vitrain became uncontrollable, showers of sparks being produced. With the latter, it was found necessary to start the combustion very slowly in a stream of air, and only to use oxygen towards the end of the operation. In each instance, the result recorded is the mean of several concordant determinations.

Each sample used for combustion analysis was dried in air during one hour at 105° . Experiments at present in progress on the rates of oxidation of the coals show that such drying would have the effect of raising their oxygen content and lowering their carbon content by less than 0.1 per cent.; moreover, the amount of alteration is approximately the same for each ingredient of the banded coal.

The Action of Solvents.—The extractions with organic solvents were made in all-glass Soxhlet apparatus, the coals being enclosed in thimbles of filter paper or alundum and held in place by plugs

of glass wool. Extraction was continued until the solvent passed over colourless, and generally for as long again. The coals were stirred at intervals, and fresh charges of solvent used from time to time. The solution obtained was filtered and distilled, and the extract freed from the last traces of solvent by evaporation on a watch-glass in a vacuum or in a stream of nitrogen, being finally allowed to remain during several weeks in a vacuum over sulphuric acid.

The coals were air-dried (at 105°) for the pyridine (1 gram), dried at 105° in the absence of air for the pyridine-chloroform (10 grams), and undried for the alcohol and chloroform (5 grams) extractions. The solvents were dry and redistilled.

The Action of Reagents.—Extractions with alcoholic potassium hydroxide were made thus: (1) One gram of coal was heated with 25 c.c. of 0.7*N*-potassium hydroxide in absolute alcohol at 80° during eight hours. The solution was diluted with water and filtered, and the alcohol evaporated. The "ulmin compounds" were then precipitated by concentrated hydrochloric acid, filtered from the solution, washed with distilled water, dried at 105° , and weighed. (2) For extraction in the cold, 1 gram of coal was allowed to remain during eight weeks in contact with 25 c.c. of 4*N*-potassium hydroxide in 75 per cent. alcohol, with frequent shaking. The amount of extracted matter was determined as in (1).

Iodine absorptions were determined by two methods. (1) The coal, weighing 0.1 gram, was placed in a 250 c.c. stoppered bottle with 25 c.c. of *N*/10-iodine in aqueous potassium iodide solution. The bottle was then shaken mechanically during the required time. The residual iodine was titrated with *N*/10-sodium thiosulphate solution (leaving the coal in suspension), using starch as indicator. (2) Iodine chloride in solution in glacial acetic acid was employed in place of aqueous iodine, using 10 c.c. of *N*/5-solution with 0.1 gram of coal.

Preliminary work with different coals showed that a considerable proportion of the iodine removed from solution by the coal was evolved on keeping in contact with sodium thiosulphate solution. This evolution was not affected to an appreciable extent by the acidity of the solution, and appeared to be of iodine merely adsorbed by the coal. The adsorbed iodine was determined by adding definite volumes of sodium thiosulphate solution in excess at intervals until no further evolution could be detected, the final titration being made at the end of twenty-four hours.

Destructive Distillation. Gaseous Products.—The method of experiment and apparatus were as described by Burgess and

Wheeler (T., 1911, **99**, 639), except that 1 gram only of coal was employed without admixture with sand.

Liquid Products.—The general arrangement of apparatus and method of carrying out the distillations were similar to those employed by Jones and Wheeler (T., 1914, **105**, 140). In the place of the spherical retort used by them, a cylindrical vessel of Jena glass, 4 cm. in diameter and 14 cm. long., was employed. This form of retort allowed of a more rapid equalisation of temperature throughout the mass of the coal than the spherical form, and permitted, in consequence, more rapid distillation. The coal (about 200 grams in weight) with which the retort was completely filled was undried, and was sieved so as to pass through a 10 and remain on a 60 mesh sieve. It was held in position, when the retort was inverted during the distillation, by a plug of glass wool.

HOME OFFICE EXPERIMENTAL STATION,
ESKMEALS.

[Received, April 30th, 1919.]

LIII.—*The Rotation-dispersion of Butyl, Heptyl, and Octyl Tartrates.*

By PERCY FARADAY FRANKLAND and FREDERIC HORACE GARNER.

ANOMALOUS rotation-dispersion is exhibited by comparatively few optically active compounds in the homogeneous state; such compounds may be conveniently classified into (1) those containing one asymmetric carbon atom, (2) those containing more than one asymmetric carbon atom, and (3) those having an absorption band in the visible part of the spectrum.

The first two of these classes and certain members of the last class exhibit a remarkable similarity in the influence which temperature and solution have on their rotation-dispersion. By examination of the circumstances in which these compounds exhibit anomalous rotation-dispersion, it is seen that in all cases *the compound becomes, or tends to become, normal in its rotation-dispersion the farther its rotation is removed from the line of zero-rotation by the effects of temperature or dilution in solution*; that is, in all cases the anomaly occurs relatively* near to the line of zero-rotation.

A high temperature-coefficient or dilution-coefficient is thus essential to the occurrence of the anomaly.

Much use has been made in recent years of the so-called "characteristic diagram" of Armstrong and Walker (*Proc. Roy. Soc.*, 1913, [A], **88**, 388) for representing the phenomena of rotation-dispersion. Such a diagram for *n*-butyl tartrate is drawn in Fig. 1A, in which are set out the specific rotations for different temperatures for the wave-lengths 4861, 5461, 5893, and 6708. It may be pointed out that in such a diagram a line is drawn at 45° to the line of zero-rotation, and on this line the rotation values for wave-length 5461 (mercury-green) are set out. Thus, for any given temperature, the position of the rotation value for λ 5461 is found on this line, and on a vertical ordinate through this point are marked the rotations at the same temperature for the other wave-lengths. After proceeding in the same way for observations made at other temperatures, the points representing the specific rotations for each wave-length are joined up by lines, which are found to be approximately straight and to intersect either in a single point or in a series of points near the line of zero-rotation.

In the above case of butyl tartrate, it will be seen that the points representing the rotations at the higher temperatures do not fall on their respective wave-length lines. This divergence is due to the maximal values for specific rotation being reached at different temperatures for different wave-lengths. The points for each wave-length thus cease to lie on a straight line when the neighbourhood of the maximum rotation is reached. Thus, in Fig. 1A especially is this the case for λ 5893 and 6708. Of course, all values for λ 5461 (mercury-green) lie by definition on the line drawn at 45° to the zero-line.

It is obvious that the same diagram may be used for similarly recording changes in rotatory dispersion brought about by solution and other influences, besides that of temperature.

The characteristic diagram, which thus serves to correlate the rotatory powers of many derivatives of similar constitution or of the same parent substance, has been successfully used by Pickard and Kenyon (*T.*, 1914, **105**, 843) to predict the conditions under which β -octyl acetate would exhibit anomalous rotation-dispersion.

For most, if not all, of the substances described by Pickard and Kenyon, the characteristic diagram represents lines (for $[\alpha]_{4350}$, $[\alpha]_{5461}$, $[\alpha]_{5893}$, and in some cases $[\alpha]_{\text{mercury-yellow}}$) which do not intersect on the line of zero-rotation, but at some distance either above or below this line. If, therefore, the characteristic diagram is really indicative of the optical properties of the compounds of which the rotation values are plotted, then, obviously, all these compounds must have anomalous rotation-dispersion when the rotation assumes a value falling between zero and the value of the rotation at the

point of intersection of these lines. Pickard and Kenyon, adopting the hypothesis of Armstrong and Walker that anomalous rotation-dispersion is always due to the presence of dynamic isomerides, ascribe the anomaly in the rotation-dispersion of some of the compounds studied by them to the fact that "the esters at low temperatures, and methyl- α -naphthylcarbinol at high temperatures, are, or tend to become, really homogeneous, as the conditions of temperature favour the existence of one only of the two isomeric forms, which have been assumed to be present" (T., 1914, 105, 1119). As a corollary of this, it would therefore follow that when optically active compounds assume rotation values between zero and that of the intersection point on the characteristic diagram, two dynamic isomerides are present.

As already pointed out by Patterson (*Trans. Faraday Soc.*, 1914, 10, 74), however, the values of the rotation in the characteristic diagram "do not necessarily have anything whatever to do with the presence or absence of dynamic isomerides"; the characteristic diagram is, in fact, a convenient method of plotting the rotation values for different wave-lengths against the rotation value for a particular wave-length. It thus affords a test as to whether the dispersion-coefficient $\Delta[a]_{\lambda_1}/\Delta[a]_{\lambda_2}$ * (Winther, *Zeitsch. physikal. Chem.*, 1903, 45, 373) is constant during the variation of the rotation, which may be brought about by (1) changes in the concentration of the active compound in solution, (2) changes of temperature, (3) changes of solvent, (4) changes caused by the combination of the active compound, and (5) changes caused by the substitution of one member of a series for another (really a special case of No. 4). By means of this method, in fact, a number of isolated observations, made under varied conditions, may be co-ordinated in one diagram.

The "rational zero," advocated by Patterson (T., 1916, 109, 1176), when used for calculating the dispersion-coefficient gives much more constant values than if the zero of rotation is used for this purpose. Moreover, the main features of the characteristic diagram are actually summarised by the values of the rational zeros and the rational dispersion-coefficients.

In the case of a single optically active compound, the characteristic diagram, in part, eliminates the *accidental* condition of the compound. On the same diagram may be co-ordinated the rotation values for different wave-lengths for a compound at different temperatures, in various concentrations, in different solvents, and

* $\Delta[a]_{\lambda_1}$ and $\Delta[a]_{\lambda_2}$ are the corresponding changes produced in the rotation for the wave-lengths λ_1 and λ_2 respectively, by varying the condition of the active compound.

even in some cases in different states of combination; thus the characteristic diagram does seem to justify its name.

Compounds, the characteristic diagram of which approach the ideal represented by the lines for different wave-lengths crossing at the same point, have always normal rotation-dispersion; in such cases, the rotation value is generally little influenced by solution, change of temperature, and substitution. In such compounds, for example, menthol and its derivatives, owing to the limited range of accessible rotation values, the rotation-dispersion cannot readily be investigated under conditions in which the characteristic diagram indicates that it would be anomalous.

At the other extreme, there are compounds of which the characteristic diagram represents lines crossing in a series of points some distance from the line of zero-rotation. In these compounds, for example, tartaric acid and its esters, the rotation is generally markedly changed by the factors of temperature, solution, and substitution; in this case, it is comparatively easy to bring the rotation to such a value that the rotation-dispersion becomes anomalous. Between these two extreme types of compounds there are, of course, intermediate types. Whilst the characteristic diagram does not represent accurately the rotation-dispersion of a compound under all conditions (see Patterson, T., 1916, 109, 1202), it nevertheless presents some advantages over previous methods of representation.

There are many facts which are difficult to explain on the hypothesis that anomalous rotation-dispersion is an indication of dynamic isomerism as postulated by Lowry and others.

Patterson (T., 1916, 109, 1204) has shown the absurdity and incompatibility of many of the hypotheses adopted in constructing formulæ to explain dynamic isomerism.

Pickard and Kenyon (T., 1915, 107, 42) have observed instances of complex rotation-dispersion with certain menthyl esters; if this is assumed to be due to the presence of dynamic isomerides, the existence of a *l*-menthyl ester having dextrorotatory power is postulated (since to produce anomalous dispersion, two substances of opposite rotatory power must be present; see Armstrong and Walker, *Trans. Faraday Soc.*, 1914, 10, 88). The great improbability of this conclusion is evident from the fact that, at present, there appears to be no record of a dextrorotatory *l*-menthyl ester.

Again, compounds of similar constitution are in the one case (a) anomalous at high temperatures and normal at low temperatures, and (b) normal at high temperatures and anomalous at low temperatures (but in each case only when the temperature-rotation curve approaches zero); dimethyl acetylchloromaleate is an example

of the first and diethyl acetylchloromaleate of the second (Walden, *Zeitsch. physikal. Chem.*, 1906, 55, 42); methyl- and hexyl-naphthylcarbinol are examples of the second case, whilst acitetrahydronaphthylcarbinol belongs to the first category (Pickard and Kenyon, T., 1914, 105, 1115, 2644, 2677).

A striking confirmation of the above views is found in the results obtained by Pickard and Kenyon (T., 1915, 107, 115). The 1-naphthoate of β -hexyl-, β -heptyl-, β -octyl-, β -decyl-, and β -undecyl-carbinols are "simple" * at high temperatures and "complex" at low temperatures, the 1-naphthoate of γ -nonyl-carbinol is "simple" at low temperatures and "complex" at high temperatures, whilst the 1-naphthoate of benzylmethylcarbinol is "simple" at all temperatures. In all these cases, if the compound exhibits "complex" rotation-dispersion, this occurs as the temperature-rotation curve approaches zero; it is particularly noteworthy that, of the above compounds, the only one that is "simple" at all temperatures has a temperature-rotation curve which never approaches zero closely. *

The test for "simple" and "complex" rotation-dispersion is unfortunately not definite in cases where a compound is "simple" at one temperature and "complex" at another temperature; at intermediate temperatures, it becomes impossible definitely to classify the rotation-dispersion according to these groups. In order to illustrate this distinction between "simple" and "complex" rotation-dispersion, we have drawn a diagram (Fig. 1B) for *n*-butyl tartrate in which $1/\alpha$ is plotted against λ^2 . It will be seen that whilst the low-temperature lines are curved, this curvature diminishes with rise of temperature, and at 165° the line becomes almost perfectly straight. This signifies that the rotation-dispersion of *n*-butyl tartrate is "complex" at low, but almost "simple" at high, temperatures.

It should be pointed out, again, that a substance of which the rotation-dispersion can be represented by the formula

$$[\alpha] = K/\lambda^2 - \lambda_0^2,$$

within the limits of experimental error, that is, is "simple," may

* The terms "simple" and "complex" are here used instead of normal and anomalous because the rotation can be more easily classified into simple and complex; on plotting the values for $1/\alpha$ against λ^2 , if a straight line results then the rotation-dispersion is simple; if a curve then the rotation-dispersion is complex. It seems advisable to retain the use of both sets of terms; thus a compound is anomalous if a maximum occurs in its rotation-dispersion curve, or is normal if no maximum is present. An anomalous compound is thus always complex, whilst a normal compound is simple or complex according to its behaviour when subjected to the above-mentioned test.

not necessarily conform to this equation with more accurate determinations of the rotation; for, as Lowry points out (*Trans. Faraday Soc.*, 1914, **10**, 57), quartz, of which the rotation-dispersion, when most accurately measured, requires three such terms, that is, is "complex," can be represented *within the same limits of accuracy as are employed in the case of optically active organic compounds* by the "simple" formula. It is, in fact, highly probable that the rotation-dispersion of optically active compounds can only be represented accurately by a series of such terms. In general, however, the constants in these terms ($K_{(n)}$ and $\lambda_{0(n)}$) are sufficiently close together for one term to suffice to express accurately enough the rotation-dispersion. When a compound, by a variation of temperature or concentration in solution, becomes "complex" in its rotation-dispersion, these constants ($K_{(n)}$ and $\lambda_{0(n)}$) (constants for the rotation-dispersion under one condition, but varying from one condition to another) have assumed such values in the several terms that these terms can no longer be united in a single term.

In the present investigation, the rotation-dispersion of *n*-butyl, *n*-heptyl, and *n*-octyl tartrates has been observed over a wide range of temperature and for a number of wave-lengths of light.

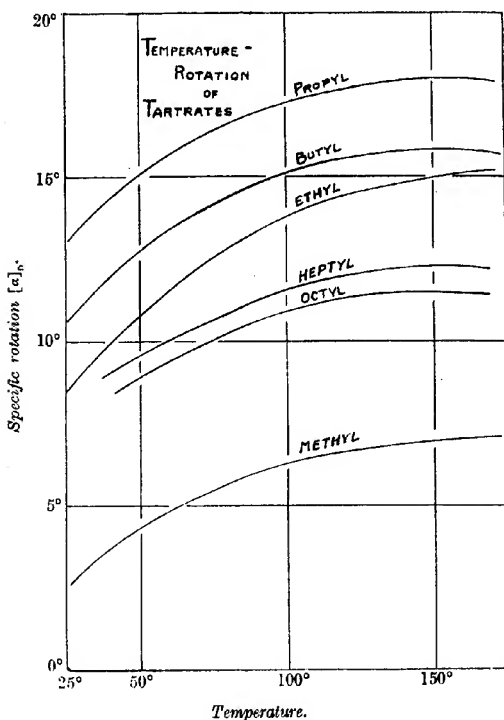
The polarimeter used was a Schmidt and Haentsch with triple field and fitted with their dispersion attachment, the illuminant being a Nernst lamp. The prism of the dispersion apparatus was calibrated by using the spectrum lines of hydrogen, mercury, and sodium; the constants of the prism for the Hartmann formula were calculated from these measurements, and hence the reading of the scale corresponding with any desired wave-length could be found. Rotations were also measured with sodium light, and these were compared with the readings obtained with the dispersion apparatus when the scale was set at the point corresponding with the mean of the sodium lines; in all cases, these readings were equal within the limits of experimental error.

The experimental error is much greater in the violet and extreme red than in the middle part of the spectrum, owing to the difficulty in measurement and also to the reduction in luminosity.

The rotation-dispersion of methyl, ethyl, and propyl tartrates has already been investigated for a wide range of temperatures by Winther and Walden. Winther (*Zeitsch. physikal. Chem.*, 1902, **41**, 161) has recorded observations from about 20° to 100°, whilst Walden (*Ber.*, 1905, **38**, 366) measured rotations from -65° to 170°. We have investigated the rotation-dispersion of butyl tartrate from 9° to 170°, and of heptyl and octyl tartrates from their melting points up to about 170°; it was found that the com-

pounds decomposed slightly at the higher temperatures, but by again taking readings at a lower temperature, it was shown that no appreciable change in the rotation had occurred. The readings of both Winther and Walden were taken with coloured lights obtained by means of light filters; more recently, Lowry and others have determined the rotation-dispersion of methyl and ethyl

FIG. 1.



tartrates at two or three temperatures for different wave-lengths of light obtained from the mercury and cadmium arcs (T., 1915, 107, 1173, 1187). The temperature-rotation curves of all these esters exhibit maxima, and for comparison, in Fig. 1, the temperature-rotation curves for sodium light for butyl, heptyl, and octyl tartrates are given, together with those obtained by Patterson (T.,

1904, 85, 765; 1913, 103, 173) for methyl, ethyl, and propyl tartrates.

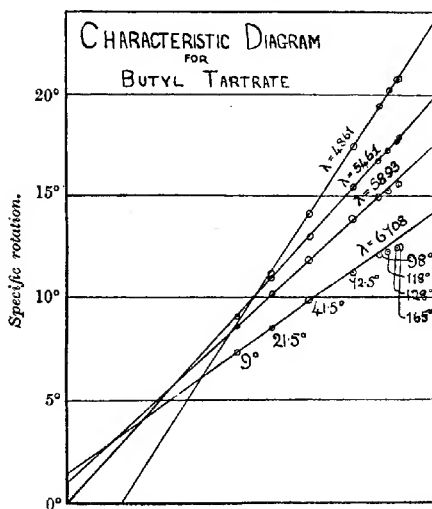
In the following table, the temperatures at which a maximum observed rotation for different wave-lengths is obtained, are recorded for the several members of the series.

TABLE I.

Maxima in Observed Rotation.

| | Red. | Yellow. | Green. | Blue. | Violet. |
|-----------------------|------|---------|--------|-------|---------|
| $\lambda =$ | 665 | 589 | 533 | 488 | 448 |
| Methyl tartrate | 160° | — | 180° | — | — |
| Ethyl " | 140 | 150° | 155 | 170° | 180° |
| Propyl " | 115 | 120 | 125 | 125 | 134 |
| Butyl " | 120 | 125 | 130 | 135 | — |
| Heptyl " | 125 | 130 | 135 | 140 | — |
| Octyl " | 125 | 130 | 135 | 140 | — |

FIG. 1A.



The values for the first three members of the series are taken from Walden (*loc. cit.*) and from Patterson (T., 1913, 103, 149, 165).

In the temperature-rotation curves for butyl, heptyl, and octyl tartrates (Figs. 2, 3, and 4 respectively), the maxima in the

specific rotation for all wave-lengths lie at temperatures above 150°.

The rotation-dispersion curves for butyl, heptyl, and octyl tartrates (Figs. 5, 6, and 7 respectively) exhibit a maximum rotation at the lower temperatures only.

The following figures show the effect of ascending the series on the rotation of the tartrates.

FIG. 1B.

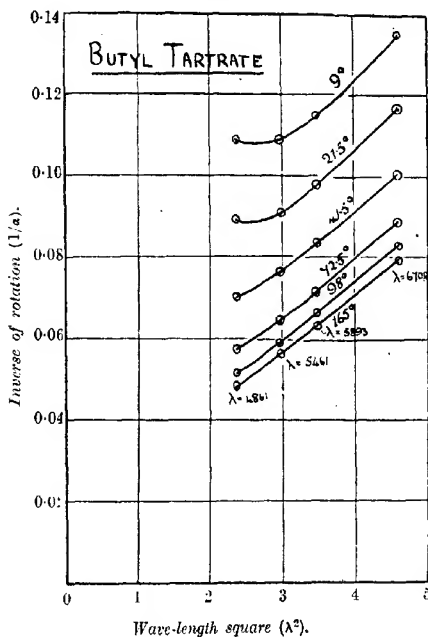


TABLE II.

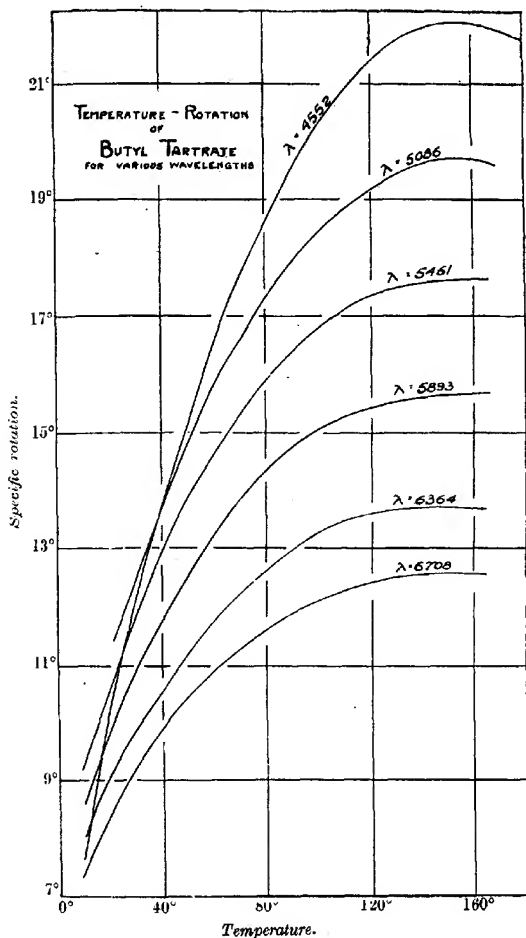
| | Methyl.* | Ethyl.* | Propyl.* | Butyl. | Heptyl. | Octyl. |
|------------------------------|----------|---------|----------|--------|---------|--------|
| $\alpha_D^{100^\circ}$ | 7.73° | 15.30° | 18.25° | 15.40° | 10.88° | 10.16° |
| $[a]_D^{100^\circ}$ | 6.18 | 13.70 | 17.20 | 15.00 | 11.44 | 10.84 |
| $[M]_D^{100^\circ}$ | 11.00 | 28.21 | 40.10 | 39.34 | 39.57 | 39.55 |

* Patterson (*loc. cit.*).

Thus in the observed and specific rotations there is a maximum at the propyl member of the series; but in the molecular rotation

the curve for the series increases until the propyl member is reached, after which it remains practically constant at about the

FIG. 2.

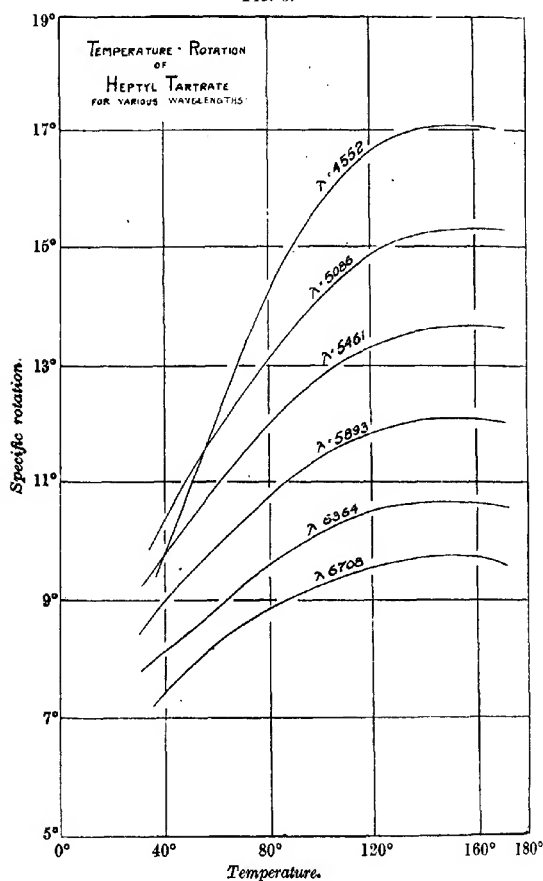


value 39.5° . It will be noticed that the maxima in the temperature-observed-rotation figures for the series (see table I) are

reached at the *lowest* temperature in the case of the propyl member.

By reference to Fig. 1, it is seen that the temperature-rotation

FIG. 3.

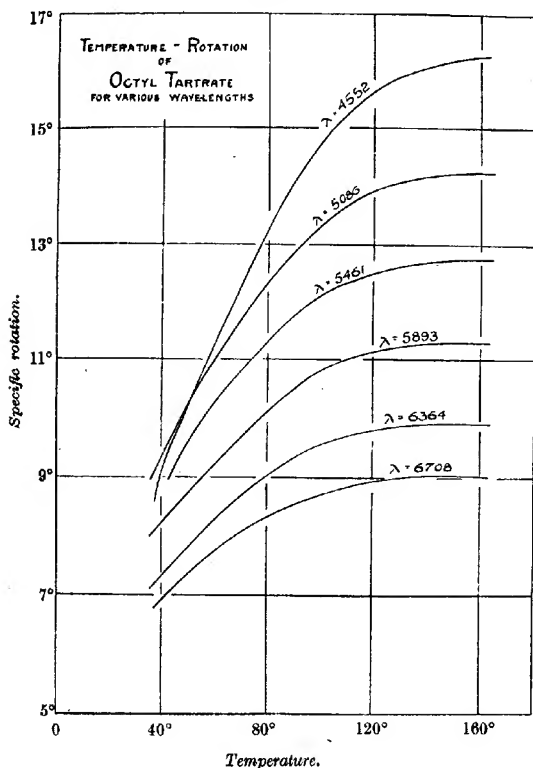


curves for sodium light for propyl, butyl, heptyl, and octyl tartrates are approximately parallel, therefore the maximum in the specific rotation occurs at about the same temperature for all these tartrates.

In Fig. 8, the molecular rotations for various coloured lights are shown for the several members of the series for a temperature of 100° ; the molecular rotation for *all colours* remains approximately constant after the propyl member is reached.

Butyl, heptyl, and octyl tartrates are "anomalous" at low

FIG. 4.



temperatures, and tend to become "normal" at high temperatures; this is readily seen by reference to Figs. 2, 3, and 4, in which the curves for the shorter wave-lengths cross the curves for the longer wave-lengths at low temperatures; the ratio, therefore, of any rotation for any wave-length to that for mercury-green

($\lambda=5461$) varies considerably at low temperatures. At higher temperatures, the figures in the following table show that the ratio tends to become constant.

FIG. 5.

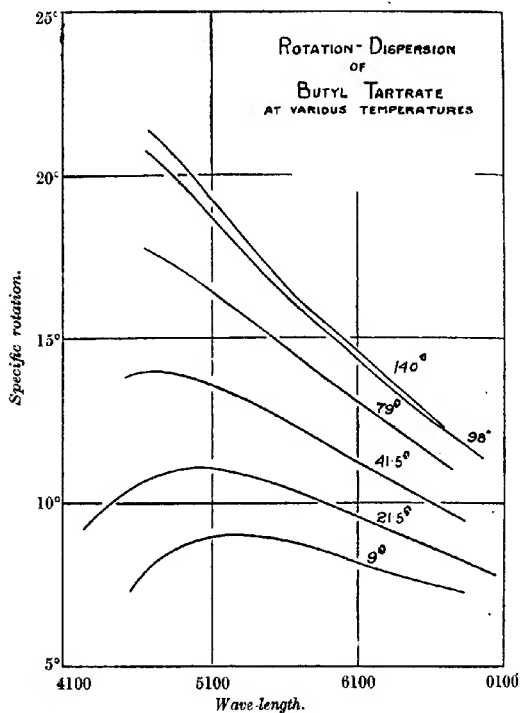


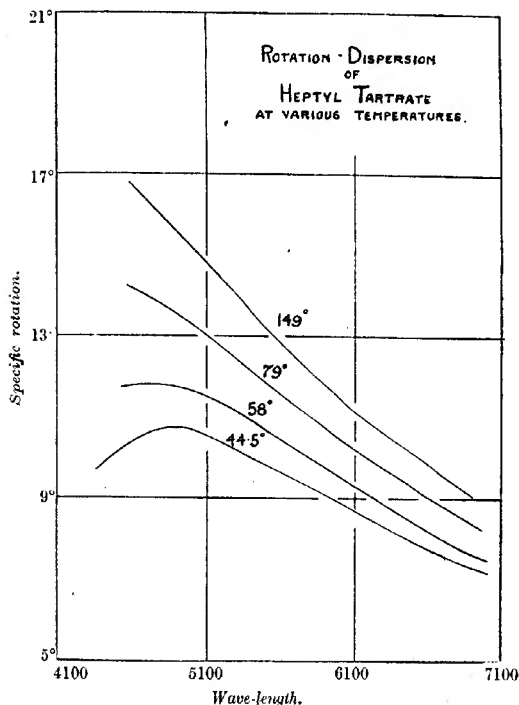
TABLE III.

| | | (Mercury Green.) | | | |
|-------------------------|-------------|------------------|-------|------|-------|
| | $\lambda =$ | 6708 | 5893 | 5461 | 5086 |
| Butyl tartrate at 21.5° | | 0.773 | 0.928 | 1.0 | 1.028 |
| " " 41.5 | | 0.758 | 0.911 | 1.0 | 1.070 |
| " " 98 | | 0.723 | 0.892 | 1.0 | 1.098 |
| " " 128 | | 0.707 | 0.888 | 1.0 | 1.119 |
| " " 165 | | 0.709 | 0.888 | 1.0 | 1.113 |
| Heptyl tartrate at 168° | | 0.707 | 0.886 | 1.0 | 1.116 |
| Octyl tartrate at 165° | | 0.707 | 0.886 | 1.0 | 1.114 |

The ratios for butyl, heptyl, and octyl tartrates for the same wave-lengths are approximately equal at the higher temperatures;

whilst these ratios are rather high, they are not sufficiently high to indicate that the esters are abnormal in their rotation-dispersion. On applying the test for "simple" and "complex" rotatory dispersion (see footnote, p. 640), however, it is found that at all temperatures the rotation-dispersion is complex, but the farther the rotation is removed from the zero line by raising the tempera-

FIG. 6.



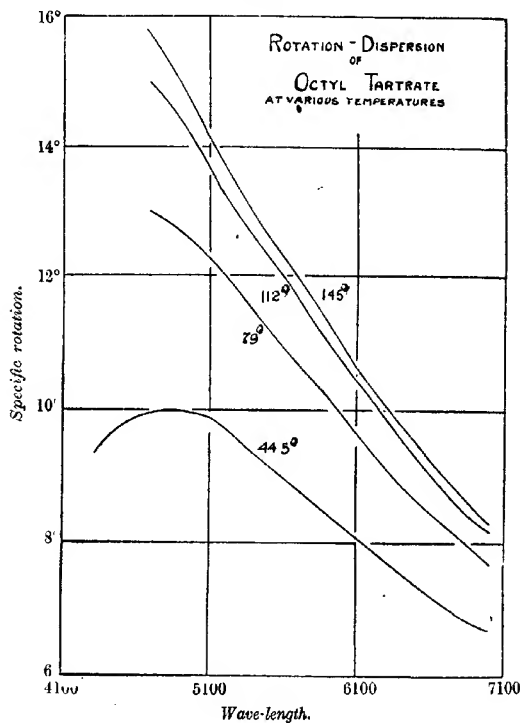
ture, the more simple (or less complex) does the rotation become; thus at high temperatures the curve $1/\alpha$ against λ^2 has only a very slight curvature, for example, see Fig. 1b.

EXPERIMENTAL.

The esters were prepared by a modification of the usual hydrochloric acid method of esterification; four molecular proportions of alcohol and one of acid were mixed and saturated with dry

hydrogen chloride while the mixture was heated on a water-bath. After leaving the mixture for a few weeks, it was again saturated with hydrogen chloride, this time in the cold; the hydrochloric acid, water, and excess of alcohol were distilled off, and the residual ester was then distilled in a partial vacuum of 12 mm. (in the case of heptyl and octyl tartrates, recrystallisation from light petroleum

FIG. 7.



was also adopted for the purification of the residual ester). By this method of esterification, an almost theoretical yield of ester (calculated on the acid used) was obtained.

In the case of heptyl tartrate, specimens were also prepared in the following ways:

(1) The mixture of acid and alcohol was saturated with hydrogen chloride in the cold, the hydrochloric acid being removed, after

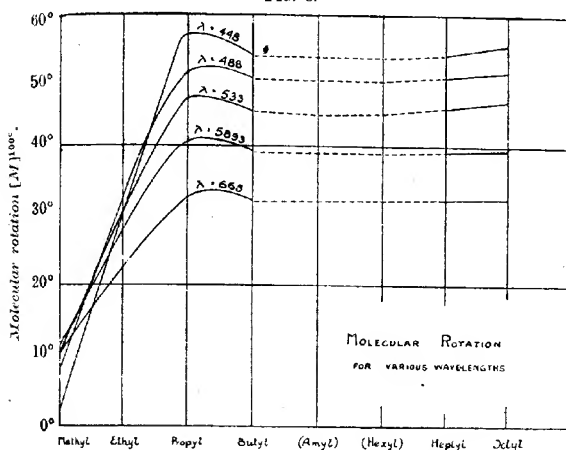
several weeks, by keeping in a desiccator; the ester crystallised out, and was recrystallised from light petroleum.

The heptyl tartrate obtained in this way had α_D^{100} 10.90° .

(2) Patterson and Dickinson's method (T., 1901, 79, 280) was employed, commencing with ethyl tartrate. The product had α_D^{100} 10.85° .

The heptyl tartrate prepared by the method given above had α_D^{100} 10.88° , and thus no appreciable racemisation is produced by this method of esterification.

FIG. 8.



n-Butyl tartrate was prepared from butyl alcohol boiling at $116.5\text{--}117^\circ/752$ mm. (The boiling point of pure *n*-butyl alcohol is $116.5\text{--}117.2^\circ/760$ mm.) After six distillations in a vacuum of 12 mm., the butyl tartrate had α_D^{25} 22.25° ($l=2$ -dm.); this rotation is slightly less than that recorded by Freundler (*Ann. Chim. Phys.*, 1893, [vii], 3, 446), namely, α_D^{25} 22.51° ($l=2$ -dm.). A specimen of butyl tartrate prepared from a slightly impure alcohol (b. p. $115\text{--}117^\circ$), however, we found to have α_D^{25} 24.64° ($l=2$ -dm.). Butyl tartrate melts at 22° (Freundler, *Bull. Soc. chim.*, 1894, [iii], 11, 309, gives $21\text{--}22^\circ$) and boils at $178^\circ/12$ mm. (Freundler gives $208^\circ/12$ mm.). It exhibits a maximum in its rotation-dispersion within the wave-lengths recorded at temperatures below 70° .

Densities.

| Temperature | 18° | 61.0° | 101.2° | 132.5° | 169.5° |
|-------------|------------|--------------|---------------|---------------|---------------|
| D_4 | 1.0968 | 1.0600 | 1.0246 | 0.9986 | 0.9654 |

BUTYL TARTRATE.

Temperature 9°. Density 1.1044.

| | | | | | | | | | |
|-------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|------|
| λ | 6563 | 6147 | 5893 | 5769 | 5679 | 5461 | 5219 | 4861 | 4562 |
| α ($l=2$ -dem.) | 16.44 | 18.39 | 19.13 | 19.48 | 19.71 | 19.98 | 20.18 | 20.47 | 20.6 |
| $[\alpha]$ | 7.44 | 8.32 | 8.67 | 8.82 | 8.92 | 9.04 | 9.13 | 9.26 | 9.3 |
| $[\alpha]$ | 19.5 | 21.85 | 22.76 | 23.14 | 23.41 | 23.73 | 23.97 | 24.31 | 24.3 |

Temperature 21.5°. Density 1.0934.

| | | | | | | | | |
|-------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| λ | 6563 | 6364 | 6147 | 6025 | 5893 | 5709 | 5679 | 5398 |
| α ($l=2$ -dem.) | 17.8 | 18.89 | 19.24 | 20.08 | 21.05 | 21.63 | 22.80 | 23.60 |
| $[\alpha]$ | 8.1 | 8.55 | 8.80 | 9.18 | 9.63 | 9.81 | 10.45 | 10.81 |
| $[\alpha]$ | 21.4 | 22.43 | 23.09 | 24.09 | 25.26 | 26.01 | 27.41 | 28.38 |
| λ | 5323 | 5219 | 5154 | 5086 | 5004 | 4925 | 4861 | 4552 |
| α ($l=2$ -dem.) | 24.00 | 24.39 | 24.59 | 24.66 | 24.61 | 24.56 | 24.40 | 23.4 |
| $[\alpha]$ | 11.08 | 11.25 | 11.27 | 11.30 | 11.28 | 11.26 | 11.23 | 10.7 |
| $[\alpha]$ | 28.86 | 29.51 | 29.57 | 29.65 | 29.59 | 29.53 | 29.46 | 28.2 |

Temperature 41.5°. Density 1.0759.

| | | | | | | | | |
|-------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| λ | 6563 | 6364 | 6147 | 6025 | 5893 | 5769 | 5679 | 5401 |
| α ($l=2$ -dem.) | 21.36 | 23.11 | 24.26 | 24.94 | 25.66 | 26.39 | 26.89 | 28.14 |
| $[\alpha]$ | 10.53 | 10.74 | 11.22 | 11.39 | 11.52 | 11.70 | 11.80 | 13.08 |
| $[\alpha]$ | 29.04 | 29.18 | 29.38 | 30.41 | 31.29 | 32.18 | 32.79 | 34.31 |
| λ | 5323 | 5219 | 5105 | 5086 | 5004 | 4861 | 4785 | 4552 |
| α ($l=2$ -dem.) | 28.71 | 29.28 | 29.83 | 30.10 | 30.22 | 30.54 | 30.6 | 30.4 |
| $[\alpha]$ | 13.34 | 13.61 | 13.86 | 13.99 | 14.04 | 14.19 | 14.2 | 14.1 |
| $[\alpha]$ | 33.01 | 33.70 | 36.38 | 36.70 | 36.85 | 37.2 | 37.3 | 37.1 |

Temperature 72.5°. Density 1.0492.

| | | | | | | |
|--------------------------------|-------|-------|-------|-------|-------|-------|
| λ | 6563 | 6364 | 6147 | 6025 | 5893 | 5769 |
| λ ($l=2$ -dem.) | 24.01 | 25.93 | 27.41 | 28.29 | 29.18 | 30.13 |
| $[\alpha]$ | 11.31 | 12.36 | 13.06 | 13.48 | 13.91 | 14.36 |
| $[\eta]$ | 30.77 | 32.42 | 34.27 | 35.37 | 36.49 | 37.69 |
| λ | 5568 | 5461 | 5219 | 5086 | 4861 | 4662 |
| λ ($l=2$ -dem.) | 31.58 | 32.41 | 34.12 | 35.09 | 36.6 | 37.6 |
| $[\alpha]$ | 15.05 | 15.44 | 16.26 | 16.72 | 17.4 | 17.9 |
| $[\eta]$ | 39.40 | 40.51 | 42.67 | 43.88 | 45.8 | 47.0 |

Temperature 98°. Density 1.0269.

| | | | | | | | |
|--------------------------------|-------|-------|-------|-------|-------|-------|-------|
| λ | 6708 | 6563 | 6364 | 6147 | 6025 | 5893 | 5769 |
| λ ($l=2$ -dem.) | 24.1 | 25.76 | 27.15 | 28.4 | 29.70 | 30.71 | 31.72 |
| $[\alpha]$ | 11.7 | 12.54 | 13.22 | 13.99 | 14.46 | 14.95 | 15.46 |
| $[\eta]$ | 30.8 | 32.91 | 34.69 | 36.72 | 37.95 | 39.23 | 40.62 |
| λ | 5461 | 5219 | 5086 | 4861 | 4662 | 4532 | 4359 |
| λ ($l=2$ -dem.) | 34.40 | 36.71 | 37.80 | 39.00 | 41.4 | 41.8 | 41.6 |
| $[\alpha]$ | 16.29 | 17.87 | 18.40 | 19.43 | 20.2 | 20.3 | 20.2 |
| $[\eta]$ | 42.73 | 46.90 | 48.29 | 50.38 | 52.9 | 53.4 | 53.1 |

Temperature 118°. Density 1.0099.

| | | | | | | | |
|--------------------------------|-------|-------|-------|-------|-------|-------|-------|
| λ | 6978 | 6563 | 6364 | 6147 | 6025 | 5893 | 5769 |
| λ ($l=2$ -dem.) | 23.2 | 25.02 | 25.91 | 27.32 | 29.00 | 31.01 | 32.10 |
| $[\alpha]$ | 11.5 | 12.39 | 12.83 | 13.53 | 14.36 | 15.35 | 15.80 |
| $[\eta]$ | 30.1 | 32.50 | 33.66 | 35.49 | 37.68 | 40.29 | 41.70 |
| λ | 5568 | 5461 | 5323 | 5219 | 5154 | 4861 | 4662 |
| λ ($l=2$ -dem.) | 33.97 | 34.97 | 36.29 | 37.14 | 37.79 | 40.82 | 42.3 |
| $[\alpha]$ | 16.82 | 17.94 | 17.97 | 18.39 | 18.71 | 20.21 | 20.9 |
| $[\eta]$ | 44.13 | 45.31 | 47.14 | 48.25 | 49.10 | 53.03 | 54.9 |

Temperature 128°. Density 1.0011.

| | | | | | | | |
|-------------------------------|-------|-------|-------|-------|-------|-------|-------|
| λ | 6708 | 6563 | 6364 | 6147 | 6025 | 5893 | 5769 |
| α ($l=1$ -dem.) | 12.4 | 12.92 | 13.64 | 14.53 | 14.97 | 15.55 | 16.10 |
| $[\alpha]$ | 12.4 | 12.91 | 13.63 | 14.51 | 14.95 | 15.63 | 16.08 |
| $[\alpha]$ | 32.5 | 33.86 | 35.75 | 38.09 | 39.24 | 40.76 | 42.20 |
| λ | 5679 | 5568 | 5461 | 5219 | 5086 | 4861 | 4785 |
| α ($l=1$ -dem.) | 16.48 | 16.99 | 17.55 | 18.67 | 19.5 | 20.4 | 21.0 |
| $[\alpha]$ | 16.46 | 16.97 | 17.53 | 18.65 | 19.5 | 20.4 | 21.0 |
| $[\alpha]$ | 43.20 | 44.53 | 46.0 | 48.92 | 51.2 | 53.5 | 55.0 |

Temperature 140°. Density 0.9906.

| | | | | | | | | |
|-------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| λ | 6708 | 6563 | 6364 | 6147 | 6025 | 5893 | 5769 | 5668 |
| α ($l=2$ -dem.) | 24.65 | 26.77 | 27.09 | 28.82 | 29.86 | 31.00 | 32.16 | 32.92 |
| $[\alpha]$ | 12.44 | 13.00 | 12.67 | 14.54 | 15.08 | 15.65 | 16.23 | 17.15 |
| $[\alpha]$ | 32.65 | 34.13 | 35.88 | 38.16 | 39.56 | 41.06 | 42.58 | 44.99 |
| λ | 5461 | 5323 | 5219 | 5154 | 5086 | 4861 | 4552 | 4346 |
| α ($l=2$ -dem.) | 34.92 | 36.42 | 37.41 | 38.01 | 38.88 | 41.14 | 42.5 | 43.6 |
| $[\alpha]$ | 17.63 | 18.36 | 18.88 | 19.18 | 19.62 | 20.76 | 21.4 | 22.0 |
| $[\alpha]$ | 46.25 | 48.24 | 49.55 | 50.34 | 51.50 | 54.49 | 56.3 | 57.7 |

| | | | | | | | | | |
|----------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| λ | 6708 | 6663 | 6364 | 6147 | 6025 | 5893 | 5769 | 5679 | 5568 |
| $a(t=1\text{-dem.})$ | 12.30 | 12.72 | 13.42 | 14.26 | 14.73 | 15.39 | 15.86 | 16.25 | 16.72 |
| $[a]$ | 12.54 | 12.97 | 13.68 | 14.54 | 15.01 | 15.69 | 16.19 | 16.57 | 17.04 |
| $[M]$ | 32.90 | 34.02 | 35.90 | 38.14 | 39.40 | 41.16 | 42.48 | 43.47 | 44.72 |
| λ | 5461 | 5323 | 5219 | 5086 | 4861 | 4662 | 4562 | 4369 | |
| $a(t=1\text{-dem.})$ | 17.30 | 17.90 | 18.41 | 19.06 | 20.12 | 21.2 | 21.6 | 22.3 | |
| $[a]$ | 17.66 | 18.24 | 18.77 | 19.43 | 20.61 | 21.6 | 22.1 | 22.7 | |
| $[M]$ | 46.32 | 47.88 | 49.24 | 50.98 | 53.82 | 56.7 | 57.9 | 59.6 | |

| | | | | | | | | | |
|----------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| λ | 6708 | 6663 | 6364 | 6147 | 6025 | 5893 | 5769 | 5679 | 5568 |
| $a(t=1\text{-dem.})$ | 12.13 | 12.59 | 13.30 | 14.14 | 14.59 | 15.20 | 15.74 | 16.15 | 16.63 |
| $[a]$ | 12.62 | 12.99 | 13.72 | 14.58 | 15.06 | 15.69 | 16.25 | 16.67 | 17.16 |
| $[M]$ | 32.85 | 34.10 | 36.02 | 38.27 | 39.51 | 41.16 | 42.63 | 43.74 | 45.04 |
| λ | 5461 | 5323 | 5219 | 5086 | 4861 | 4662 | 4562 | 4454 | |
| $a(t=1\text{-dem.})$ | 17.12 | 17.85 | 18.38 | 19.05 | 19.96 | 21.2 | 21.6 | 22.4 | |
| $[a]$ | 17.67 | 18.42 | 18.97 | 19.66 | 20.60 | 21.9 | 22.3 | 23.1 | |
| $[M]$ | 46.36 | 48.34 | 49.78 | 51.39 | 54.05 | 57.4 | 58.6 | 60.7 | |

Temperature 151°. Density 0.981.

| | | | | | | | | | |
|----------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| λ | 6708 | 6663 | 6364 | 6147 | 6025 | 5893 | 5769 | 5679 | 5568 |
| $a(t=1\text{-dem.})$ | 12.13 | 12.59 | 13.30 | 14.14 | 14.59 | 15.20 | 15.74 | 16.15 | 16.63 |
| $[a]$ | 12.62 | 12.99 | 13.72 | 14.58 | 15.06 | 15.69 | 16.25 | 16.67 | 17.16 |
| $[M]$ | 32.85 | 34.10 | 36.02 | 38.27 | 39.51 | 41.16 | 42.63 | 43.74 | 45.04 |
| λ | 5461 | 5323 | 5219 | 5086 | 4861 | 4662 | 4562 | 4454 | |
| $a(t=1\text{-dem.})$ | 17.12 | 17.85 | 18.38 | 19.05 | 19.96 | 21.2 | 21.6 | 22.4 | |
| $[a]$ | 17.67 | 18.42 | 18.97 | 19.66 | 20.60 | 21.9 | 22.3 | 23.1 | |
| $[M]$ | 46.36 | 48.34 | 49.78 | 51.39 | 54.05 | 57.4 | 58.6 | 60.7 | |

Temperature 165°. Density 0.969.

n-Heptyl tartrate, $C_{18}H_{34}O_6$, which has not previously been described, was prepared from heptyl alcohol boiling at 175–176° (pure heptyl alcohol boils at 175.5°). It melts at 35–35.5° and boils at 228°/12 mm. and 235°/14 mm. It has n_D^{20} 1.4176 ($l=2$ dm.). Its rotation-dispersion curves exhibit maxima between the wave-lengths recorded for temperatures below 70°. It was found impossible to supercool heptyl and octyl tartrates below more than 5° of their melting points without crystallisation occurring.

Densities.

| | | | | |
|----------------------|--------|--------|--------|--------|
| Temperature | 41.0° | 67.1° | 105.3° | 131.1° |
| D _r | 0.9985 | 0.9776 | 0.9473 | 0.9283 |

| | | Temperature 100°. Density 0.9520. | | | |
|-----------------------------------|-------|-----------------------------------|-------|-------|-------|
| λ | 6708 | 6363 | 6364 | 6147 | 5893 |
| α ($l=2$ -dem.) | 17-06 | 18-27 | 19-32 | 20-40 | 21-76 |
| [α] | 9-27 | 9-59 | 10-15 | 10-71 | 11-33 |
| [M] | 32-15 | 33-26 | 33-17 | 33-14 | 33-61 |
| λ | 5461 | 5323 | 5219 | 5154 | 5004 |
| α ($l=2$ -dem.) | 24-34 | 25-24 | 25-90 | 26-35 | 27-24 |
| [α] | 12-79 | 13-26 | 13-60 | 13-84 | 14-31 |
| [M] | 44-31 | 45-95 | 47-15 | 47-97 | 48-68 |
| Temperature 110°. Density 0.9442. | | | | | |
| λ | 6708 | 6363 | 6364 | 6147 | 5893 |
| α ($l=2$ -dem.) | 17-02 | 18-50 | 19-33 | 20-66 | 21-34 |
| [α] | 9-49 | 9-84 | 10-34 | 10-94 | 11-30 |
| [M] | 32-89 | 34-12 | 35-85 | 37-92 | 39-17 |
| λ | 5461 | 5323 | 5219 | 5154 | 5004 |
| α ($l=2$ -dem.) | 24-82 | 25-78 | 26-74 | 27-15 | 27-58 |
| [α] | 13-14 | 13-65 | 14-16 | 14-38 | 14-60 |
| [M] | 45-66 | 47-32 | 49-08 | 49-83 | 50-62 |
| Temperature 125°. Density 0.9328. | | | | | |
| λ | 6708 | 6363 | 6364 | 6147 | 6023 |
| α ($l=2$ -dem.) | 18-03 | 18-66 | 19-66 | 20-82 | 21-54 |
| [α] | 9-66 | 10-00 | 10-54 | 11-16 | 11-56 |
| [M] | 33-50 | 34-68 | 36-52 | 38-68 | 40-02 |
| λ | 5368 | 5461 | 5219 | 5154 | 5086 |
| α ($l=2$ -dem.) | 24-42 | 25-15 | 26-98 | 27-66 | 28-04 |
| [α] | 13-09 | 13-48 | 14-46 | 14-83 | 15-03 |
| [M] | 45-37 | 46-72 | 50-12 | 51-39 | 52-09 |

5879
23-09
12-12
42-0
43-11
44-54
4662
29-7
15-2
52-7

5769
22-88
11-81
41-92
4861
28-10
14-76
51-15

5679
23-40
12-39
42-95
44-24
4662
30-4
16-1
55-9

5769
22-86
12-11
41-96
4861
28-77
15-24
52-8

5679
23-72
12-71
44-07
4662
30-8
16-6
57-2

5893
22-32
11-96
41-47
5004
28-60
15-33
53-13

Temperature 134°. Density 0.9258.

| | | | | | | | | |
|-------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| λ | 6563 | 6364 | 6147 | 6025 | 5893 | 5769 | 5679 | 5568 |
| α ($l=2$ -dem.) | 18.69 | 19.75 | 20.83 | 21.59 | 22.36 | 23.10 | 23.63 | 24.39 |
| $[\alpha]$ | 10.10 | 9.75 | 11.25 | 11.66 | 12.07 | 12.48 | 12.76 | 13.17 |
| $[\eta]$ | 34.98 | 36.97 | 38.99 | 40.41 | 41.85 | 43.24 | 44.23 | 45.66 |
| λ | 5323 | 5219 | 5154 | 5086 | 5004 | 4861 | 4662 | 4359 |
| α ($l=2$ -dem.) | 26.16 | 26.90 | 27.49 | 28.00 | 28.69 | 29.60 | 30.7 | 32.1 |
| $[\alpha]$ | 14.13 | 14.33 | 14.85 | 15.12 | 15.49 | 15.96 | 16.6 | 17.3 |
| $[\eta]$ | 48.97 | 50.35 | 51.49 | 52.41 | 53.71 | 55.41 | 57.5 | 60.1 |

Temperature 149°. Density 0.914.

| | | | | | | | | |
|-------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| λ | 6563 | 6364 | 6147 | 6025 | 5893 | 5769 | 5679 | 5568 |
| α ($l=1$ -dem.) | 9.30 | 9.79 | 10.37 | 10.73 | 11.10 | 11.52 | 11.77 | 12.18 |
| $[\alpha]$ | 10.17 | 10.71 | 11.35 | 11.74 | 12.14 | 12.60 | 12.88 | 13.33 |
| $[\eta]$ | 35.2 | 37.05 | 39.25 | 40.6 | 42.0 | 43.6 | 44.55 | 46.1 |
| λ | 5323 | 5219 | 5154 | 5086 | 5004 | 4861 | 4662 | 4359 |
| α ($l=1$ -dem.) | 13.16 | 13.50 | 13.81 | 14.06 | 14.34 | 14.79 | 15.4 | 16.2 |
| $[\alpha]$ | 14.40 | 14.77 | 15.11 | 15.38 | 15.69 | 16.18 | 16.9 | 17.7 |
| $[\eta]$ | 49.8 | 51.1 | 52.25 | 53.2 | 54.25 | 56.0 | 58.5 | 61.3 |

Temperature 168°. Density 0.8995.

| | | | | | | | | |
|-------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| λ | 6563 | 6364 | 6147 | 6025 | 5893 | 5769 | 5679 | 5568 |
| α ($l=2$ -dem.) | 18.10 | 19.12 | 20.33 | 21.00 | 21.80 | 22.65 | 23.17 | 23.91 |
| $[\alpha]$ | 10.06 | 10.63 | 11.30 | 11.67 | 12.12 | 12.59 | 12.88 | 13.29 |
| $[\eta]$ | 34.89 | 36.84 | 39.17 | 40.46 | 42.00 | 43.64 | 44.64 | 46.06 |
| λ | 5323 | 5219 | 5154 | 5086 | 5004 | 4861 | 4662 | 4359 |
| α ($l=2$ -dem.) | 25.53 | 26.41 | 27.03 | 27.49 | 28.19 | 29.15 | 30.3 | 31.4 |
| $[\alpha]$ | 14.19 | 14.68 | 15.03 | 15.47 | 15.90 | 16.4 | 16.8 | 17.4 |
| $[\eta]$ | 46.10 | 50.88 | 52.68 | 52.96 | 54.31 | 56.16 | 58.4 | 60.6 |

n-Octyl tartrate, $C_{20}H_{38}O_6$, was prepared from octyl alcohol boiling at $194-195.5^\circ$ (pure *n*-octyl alcohol boils at 195°). It melts at $41-42^\circ$ and boils at $252^\circ/16$ mm. It has α_D^{100} 20.32° ($l=2$ -dm.).

A maximum is present in the rotation-dispersion curve at 45° .

Densities.

| | | Temperature 54.1° | | 73.5° | | 100.3° | | 135.1° | |
|---------------------------|-------|--------------------------|-------|-----------------|-------|------------------------|-------|-----------------|-------|
| D_4^{20} | | 0.9746 | | 0.9601 | | 0.9380 | | 0.9112 | |
| λ | 5563 | 5679 | 5769 | 5679 | 5668 | 5679 | 5679 | 5668 | |
| α ($l=2$ -dm.) .. | 17.44 | 17.44 | 17.13 | 20.54 | 21.10 | 20.58 | 21.09 | 21.67 | |
| $[\alpha]$ | 8.88 | 8.73 | 8.73 | 10.75 | 11.05 | 10.72 | 11.13 | 11.44 | |
| $[\alpha]$ | 34.02 | 33.28 | 32.69 | 40.29 | 41.39 | 47.67 | 41.71 | 42.86 | |
| λ | 4359 | 4662 | 4861 | 4662 | 4662 | 4662 | 4662 | 4662 | |
| α ($l=2$ -dm.) .. | 18.4 | 19.5 | 19.60 | 24.30 | 24.8 | 24.30 | 24.33 | 24.74 | |
| $[\alpha]$ | 9.4 | 9.9 | 9.98 | 12.31 | 12.53 | 12.53 | 12.70 | 12.84 | |
| $[\alpha]$ | 35.1 | 37.3 | 37.4 | 46.94 | 46.94 | 46.94 | 48.11 | 48.92 | |
| | | Temperature 79° | | Density 0.9551. | | Temperature 89° | | Density 0.9473. | |
| λ | 5563 | 6364 | 6147 | 6025 | 5893 | 6563 | 6364 | 6147 | 6025 |
| α ($l=2$ -dm.) .. | 15.88 | 16.40 | 17.24 | 18.23 | 18.40 | 16.75 | 17.66 | 18.69 | 19.27 |
| $[\alpha]$ | 8.32 | 8.59 | 9.02 | 9.54 | 9.84 | 8.84 | 9.32 | 9.86 | 10.17 |
| $[\alpha]$ | 31.15 | 32.17 | 33.82 | 35.76 | 36.88 | 33.13 | 34.93 | 36.96 | 38.11 |
| λ | 5461 | 5323 | 5219 | 5154 | 5086 | 5323 | 5219 | 5154 | 5086 |
| α ($l=2$ -dm.) .. | 18.24 | 18.65 | 19.06 | 19.26 | 19.36 | 22.96 | 23.74 | 24.06 | 24.33 |
| $[\alpha]$ | 9.29 | 9.50 | 9.71 | 9.86 | 9.93 | 11.64 | 12.02 | 12.53 | 12.70 |
| $[\alpha]$ | 34.8 | 35.6 | 36.37 | 36.76 | 36.95 | 43.62 | 45.04 | 46.95 | 48.11 |
| λ | 6708 | 6563 | 6364 | 6147 | 6025 | 6078 | 6563 | 6364 | 6147 |
| α ($l=2$ -dm.) .. | 15.88 | 16.40 | 17.24 | 18.23 | 18.40 | 16.18 | 16.75 | 17.66 | 18.69 |
| $[\alpha]$ | 8.32 | 8.59 | 9.02 | 9.54 | 9.84 | 8.54 | 8.84 | 9.32 | 9.86 |
| $[\alpha]$ | 31.15 | 32.17 | 33.82 | 35.76 | 36.88 | 32.00 | 33.13 | 34.93 | 36.96 |
| λ | 5461 | 5323 | 5219 | 5154 | 5086 | 5461 | 5323 | 5219 | 5154 |
| α ($l=2$ -dm.) .. | 21.63 | 22.24 | 22.96 | 23.30 | 23.52 | 22.96 | 23.74 | 24.06 | 24.33 |
| $[\alpha]$ | 11.32 | 11.64 | 12.02 | 12.20 | 12.31 | 12.12 | 12.53 | 12.70 | 12.84 |
| $[\alpha]$ | 42.43 | 43.62 | 45.04 | 45.70 | 46.14 | 45.42 | 46.95 | 47.58 | 48.11 |
| λ | 6708 | 6563 | 6364 | 6147 | 6025 | 6078 | 6563 | 6364 | 6147 |
| α ($l=2$ -dm.) .. | 16.18 | 16.75 | 17.66 | 18.69 | 19.27 | 16.18 | 16.75 | 17.66 | 18.69 |
| $[\alpha]$ | 8.54 | 8.84 | 9.32 | 9.86 | 10.17 | 8.54 | 8.84 | 9.32 | 9.86 |
| $[\alpha]$ | 32.00 | 33.13 | 34.93 | 36.96 | 38.11 | 32.00 | 33.13 | 34.93 | 36.96 |
| λ | 5461 | 5323 | 5219 | 5154 | 5086 | 5461 | 5323 | 5219 | 5154 |
| α ($l=2$ -dm.) .. | 22.28 | 22.96 | 23.74 | 24.06 | 24.33 | 22.28 | 22.96 | 23.74 | 24.06 |
| $[\alpha]$ | 11.76 | 12.12 | 12.53 | 12.70 | 12.84 | 11.76 | 12.12 | 12.53 | 12.70 |
| $[\alpha]$ | 44.06 | 45.42 | 46.95 | 47.58 | 48.11 | 44.06 | 45.42 | 46.95 | 47.58 |

Temperature 112°. Density 0.9292.

| | | | | | | | |
|-------------------------------|-------|-------|-------|-------|-------|-------|-------|
| λ | 6364 | 6147 | 6025 | 5893 | 5769 | 5679 | 5568 |
| α ($l=2$ -dcm.) | 18.12 | 19.24 | 19.88 | 20.56 | 21.26 | 21.80 | 22.44 |
| $[\alpha]$ | 9.26 | 10.35 | 10.70 | 11.06 | 11.44 | 11.73 | 12.07 |
| $[\alpha]$ | 34.08 | 38.81 | 40.08 | 41.47 | 42.87 | 43.95 | 45.24 |
| $[\alpha]$ | 33.35 | 36.53 | | | | | |
| λ | 5323 | 5219 | 5154 | 5004 | 4861 | 4662 | |
| α ($l=2$ -dcm.) | 23.82 | 24.76 | 25.25 | 26.04 | 26.94 | 27.9 | |
| $[\alpha]$ | 12.81 | 13.32 | 13.59 | 14.01 | 14.50 | 15.0 | |
| $[\alpha]$ | 48.23 | 50.91 | 51.53 | 52.50 | 54.32 | 56.3 | |
| $[\alpha]$ | 46.54 | 49.92 | | | | | |

Temperature 132°. Density 0.9140.

| | | | | | | | |
|-------------------------------|-------|-------|-------|-------|-------|-------|-------|
| λ | 6364 | 6147 | 6025 | 5893 | 5769 | 5679 | 5568 |
| α ($l=2$ -dcm.) | 18.11 | 19.21 | 19.86 | 20.59 | 21.30 | 21.82 | 22.49 |
| $[\alpha]$ | 9.39 | 10.51 | 10.87 | 11.26 | 11.65 | 11.93 | 12.30 |
| $[\alpha]$ | 35.20 | 39.38 | 40.71 | 42.20 | 43.66 | 44.72 | 46.10 |
| $[\alpha]$ | 33.88 | 37.12 | | | | | |
| λ | 5323 | 5219 | 5154 | 5004 | 4861 | 4662 | |
| α ($l=2$ -dcm.) | 23.89 | 24.80 | 25.20 | 26.35 | 27.34 | 28.5 | |
| $[\alpha]$ | 13.68 | 13.57 | 13.78 | 14.08 | 14.42 | 15.6 | |
| $[\alpha]$ | 48.97 | 50.83 | 51.65 | 52.76 | 54.04 | 55.5 | |
| $[\alpha]$ | 47.49 | | | | | | |

Temperature 145°. Density 0.9035.

| | | | | | | | |
|-------------------------|-------|-------|-------|-------|-------|-------|-------|
| λ | 6364 | 6147 | 6025 | 5893 | 5769 | 5679 | 5568 |
| α ($l=2$ -dem.) | 17.01 | 19.11 | 19.77 | 20.50 | 21.20 | 21.71 | 22.41 |
| $[\alpha]$ | 9.41 | 10.58 | 10.94 | 11.34 | 11.73 | 12.01 | 12.40 |
| $[\alpha]$ | 33.27 | 39.63 | 40.99 | 42.51 | 43.96 | 45.02 | 46.47 |
| λ | 5323 | 5219 | 5154 | 5086 | 4981 | 4862 | |
| α ($l=2$ -dem.) | 23.01 | 24.69 | 25.15 | 25.96 | 27.24 | 28.5 | |
| $[\alpha]$ | 13.22 | 13.66 | 13.92 | 14.20 | 15.07 | 15.8 | |
| $[\alpha]$ | 49.54 | 51.20 | 52.15 | 53.20 | 54.27 | 55.48 | |

Temperature 163°. Density 0.887.

| | | | | | | | |
|-------------------------|-------|-------|-------|-------|-------|-------|-------|
| λ | 6364 | 6147 | 6025 | 5893 | 5769 | 5679 | 5568 |
| α ($l=2$ -dem.) | 16.70 | 18.70 | 19.39 | 20.10 | 20.82 | 21.39 | 22.09 |
| $[\alpha]$ | 9.41 | 10.54 | 10.93 | 11.33 | 11.74 | 12.06 | 12.45 |
| $[\alpha]$ | 35.27 | 37.28 | 39.50 | 40.96 | 43.98 | 45.18 | 46.66 |
| λ | 5323 | 5219 | 5154 | 5086 | 4981 | 4862 | |
| α ($l=2$ -dem.) | 23.59 | 24.37 | 24.85 | 25.28 | 26.68 | 28.4 | |
| $[\alpha]$ | 13.30 | 13.74 | 14.01 | 14.25 | 15.04 | 16.0 | |
| $[\alpha]$ | 49.83 | 51.47 | 52.49 | 53.40 | 56.37 | 60.0 | |

CHEMICAL DEPARTMENT,
UNIVERSITY, BIRMINGHAM.

[Received, February 13th, 1919.]

LIV.—*The Tannin of the Canadian Hemlock* (*Tsuga Canadensis*, Carr.).

By RODGER JAMES MANNING and MAXIMILIAN NIERENSTEIN.

ALTHOUGH the chemistry of the pyrogallol tannins, of which gallotannin is the best known representative, has progressed during the last fifteen years, little or nothing has been published on the catechol (phlobaphen-producing) tannins, to which group nearly all the technically important vegetable tanning materials belong. We have investigated hemlock tannin, a representative of this group, in view of its colonial importance; and have accumulated observations during the three and a-half years this work has been in progress which we describe in this paper, without, however, attempting to draw any conclusions as to the probable constitution of hemlock tannin. Those who are acquainted with the literature on gallotannin (compare Dekker, "De Looistoffen," 1906; Nierenstein, "Chemie der Gerbstoffe," 1910; Dekker, "Die Gerbstoffe," 1913; Perkin and Everest, "The Natural Organic Colouring Matters," 1918) will be struck by the numerous formulae which have been suggested for gallotannin, and the contradictory results that have been obtained. This is due to the amorphous character of gallotannin in particular and the tannins in general, and it is for this reason that we give our results on hemlock tannin without committing ourselves at this juncture to any theoretical discussion on the subject.

Böttlinger's Bromo-hemlock Tannin.

Böttlinger (*Ber.*, 1884, 17, 1041) examined the action of bromine on tannin extracts, and determined the percentage of bromine contained in the precipitated bromo-compounds. On the basis of the bromo-compounds obtained from mangrove, hemlock, quebracho, mimosa, chestnut, *Terra japonica*, and spruce, he proposed formulæ for these tannins which are more or less generally accepted. Böttlinger's formula for hemlock tannin is $C_{20}H_{18}O_{10}$; he deduced this from his bromo-derivative, $C_{20}H_{14}O_{10}Br_4$, from which he also prepared the acetyl derivative, $C_{20}H_8O_{10}Br_4Ac_5$. We have made a careful re-investigation of Böttlinger's work on hemlock tannin, with the following results:

(1) Böttlinger's bromination method does not always yield the same product, $C_{20}H_{14}O_{10}Br_4$, which requires $Br=43.60$ per cent.

but a series of compounds in which the bromine content varies from 40 to 49 per cent. The analyses of eleven preparations gave:

Br = 41.28, 47.56, 43.88, 40.12, 43.20, 47.29, 44.56, 41.74, 48.48, 41.56, and 43.26 per cent.

(2) If Böttinger's product is obtained, it can be fractionated into a number of compounds in which the bromine content varies from 40 to 48 per cent. The fractionation method employed by us consisted in dissolving the bromo-compound in acetone and fractionally precipitating by the addition of chloroform. Three such experiments were made, and the results were:

Experiment I.—Bromine content of product, 43.12 per cent.

| Fractions: | I. | II. | III. | IV. | V. |
|------------|-------|-------|-------|-------|-----------------|
| Br = | 43.56 | 45.03 | 46.82 | 46.96 | 48.09 per cent. |

Experiment II.—Bromine content of product, 43.88 per cent.

| Fractions: | I. | II. | III. | IV. | V. |
|------------|-------|-------|-------|-------|-----------------|
| Br = | 40.22 | 42.84 | 44.22 | 47.86 | 48.56 per cent. |

Experiment III.—Bromine content of product, 43.98 per cent

| Fractions: | I. | II. | III. |
|------------|-------|-------|-----------------|
| Br = | 41.98 | 44.56 | 46.22 per cent. |

(3) If hemlock tannin is prepared and fractionated by the method described later, and the different fractions are brominated separately, a series of bromo-compounds is obtained in which the bromine content increases as the phlobaphen content decreases.

| Brominated Phlobaphens. | | | Brominated Hemlock Tannin. | | | |
|-------------------------|-------|--------|----------------------------|-------|-------|--------|
| Fractions: | I. | II. | Fractions: | I. | III. | V. |
| Br = | 38.59 | 42.33% | Br = | 43.56 | 46.82 | 47.40% |
| Br = | 39.14 | 41.56% | Br = | — | 46.77 | 48.09% |
| Br = | 40.11 | 42.82% | Br = | — | 46.96 | 48.22% |
| Br = | — | — | Br = | — | — | 49.56% |

Our results suggest that Böttinger's formula for hemlock tannin and bromo-hemlock tannin must be disregarded, which conclusion, probably, also applies to the other bromo-tannins mentioned.

Alkali Hydrolysis of Bromo-hemlock Tannin.

During his investigations on bromo-quebracho tannin, Nierenstein (*Collegium*, 1905, 69) obtained on hydrolysis with alcoholic potassium hydroxide (1) isovanillic acid, and (2) a substance, $C_8H_7O_4Br$, to which he assigned provisionally the name monobromo-quebrachilic acid. The latter crystallised from chloroform in small needles melting at 119—120°. We have extended these investi-

gations to bromo-hemlock tannin, but were only able to isolate a substance, $C_5H_7O_4Br$, which apparently is closely allied to monobromoquebrachilic acid, and is provisionally called *monobromotsuginic acid*. For comparison, the melting points of these two substances and of their derivatives are tabulated.

| <i>Monobromoquebrachilic Acid.</i> | | <i>Monobromotsuginic Acid.</i> | |
|------------------------------------|----------------|--------------------------------|----------------|
| Free acid ... | m. p. 119—120° | Free acid ... | m. p. 143—145° |
| Methyl ester ... | m. p. 96—98° | Methyl ester ... | m. p. 108—111° |
| Ethyl ester... | m. p. 93—94° | Ethyl ester ... | m. p. 100—102° |

Nierenstein (*loc. cit.*) obtained from monobromoquebrachilic acid on further hydrolysis monobromoresorcinol, but we have failed to isolate any definite disintegration product from monobromotsuginic acid.

Alkali Hydrolysis.—About 10 grams of bromo-hemlock tannin containing 44.56 per cent. of bromine were heated under reflux on a water-bath with 100 c.c. of 20 per cent. alcoholic potassium hydroxide for six hours, and the solution was filtered after dilution with water. The filtrate was evaporated to dryness and extracted with acidified boiling alcohol. After several days, a crop of needles (about 0.1 gram) was obtained, which was collected and recrystallised from alcohol and benzene. Repetition of the hydrolysis gave amounts of crude monobromotsuginic acid varying from 0.7 to 1.2 per cent. of the weight of bromo-hemlock tannin.

Monobromotsuginic acid crystallises from alcohol and benzene in small, sharp needles which melt at 143—145°, carbon dioxide being evolved.

Found: C=38.75; H=3.42; Br=31.62. M.W.=251.

$C_5H_7O_4Br$ requires C=38.87; H=2.87; Br=32.39 per cent.
M.W.=247.

The *methyl* ester, prepared by the hydrochloric acid method, crystallises from chloroform in silky needles melting at 108—111°.

Found: C=41.95; H=3.67.

$C_5H_9O_4Br$ requires C=41.38; H=3.44 per cent.

The *ethyl* ester crystallises from alcohol in needles melting at 100—102°.

Found: C=43.22; H=4.58.

$C_{10}H_{11}O_4Br$ requires C=43.63; H=4.00 per cent.

The *acetyl* derivative is prepared by digesting monobromotsuginic acid with acetic anhydride for several hours, the excess of acetic anhydride being removed in a vacuum. It separates from

alcohol in small, cubic crystals melting at 124--126°, carbon dioxide being evolved.

Found: C=41.22; H=3.64.

$C_{10}H_9O_5Br$ requires C=41.52; H=3.12 per cent.

Attempts to prepare carbethoxy- and benzoyl derivatives failed, as the products did not crystallise.

So far as it is possible to deduce from the above data, monobromotsuginic acid may be regarded as having the constitution $CO_2H \cdot C_7H_5OBr \cdot OH$.

Much work, however, is still required before it will be possible to decide on a definite constitution for this fission product, which in time may prove of importance to the chemistry of hemlock tannin in particular and the catechol tannins in general.

Preparation of Hemlock Tannin.

The finely sieved hemlock bark (about 8 kilos. were used each time) was extracted repeatedly with acetone. The extraction must always be carried out in the cold, on account of the ease with which hemlock tannin is oxidised to phlobaphens. The united acetone solutions were evaporated to one-third of their bulk under diminished pressure at about 55°. In this and in the succeeding operations, great care must be taken to keep the temperature as low as possible, as otherwise a considerable loss of hemlock tannin occurs through the formation of phlobaphen.

In order to precipitate the phlobaphens, the concentrated acetone solution was poured into twice its bulk of water and allowed to remain overnight. The phlobaphens, which appeared as a bulky, dark red mass, were collected, washed, and dried in a desiccator. The filtrate, which contained the hemlock tannin and always a certain amount of unprecipitated phlobaphens, was evaporated to a viscid mass in a vacuum at a temperature not exceeding 55°. This was dissolved in 570 c.c. of alcohol, and if still rich in phlobaphens gave a further precipitation if diluted with an equal amount of water. Usually, only a small portion of the alcoholic solution was tested, so as to avoid loss through oxidation. If, then, on adding water to a test portion little or no precipitation of phlobaphens took place, the whole alcoholic solution was evaporated to dryness under diminished pressure at 55°. On the other hand, if much phlobaphen was precipitated, the solution was diluted with an equal amount of water, and the preceding operations were repeated. The resultant mass (about 300 grams) was

carefully dried, and appeared then as a dark red, brittle substance, evidently still rich in phlobaphens.

The crude hemlock tannin (100 grams) was extracted with 750 c.c. of carefully dried acetone. The acetone was added in several portions and filtered before each fresh addition. The residue insoluble in acetone appeared, when carefully washed, with light petroleum and dried in a vacuum at 70°, as a pale brown powder, which weighed about 5 grams. The dark red acetone solution was treated with portions of 50, 100, and 400 c.c. of chloroform, as used by Nierenstein in the purification of gallotannin (*Annalen*, 1912, **388**, 243). The first two fractions were dark and inclined to be viscid. The third fraction was pink. When washed with light petroleum and dried in a vacuum, they weighed respectively 8, 12, and 35 grams. The filtrate from fraction III was evaporated to dryness under diminished pressure at 55°, and the residue dissolved in 150 c.c. of ethyl acetate, which when poured into 200 c.c. of chloroform yielded 26 grams of a light-coloured precipitate. The filtrate was again evaporated to dryness, the residue dissolved in 100 c.c. of ethyl acetate, and fractions V and VI were precipitated by successive addition of 100 c.c. of chloroform. Fraction V (10 grams) was faintly pink, whilst fraction VI (2 grams) was creamy-white.

Found:

Fraction III.—C=61.58, 61.86; H=5.05, 5.29.

Fraction IV.—C=63.52, 63.30; H=5.31, 5.33.

Fraction V.—C=64.09; H=5.41.

Fraction VI.—C=64.24, 64.06, 64.33; H=4.88, 5.08, 5.23 per cent.

The amorphous character of the products and also the variations in the composition of the different fractions show how undesirable it is to calculate an empirical formula for hemlock tannin, as is also the case with gallotannin (compare Nierenstein, *Annalen*, 1912, **388**, 243). In addition to this, hemlock tannin also contains traces of a methoxy-compound, from which we have not succeeded in freeing it. We found that even the purest fraction (VI) contained OMe=0.80, whilst some of the other fractions gave as much as 3.56 per cent. of methoxyl.*

* During these investigations, experiments were also made to see if some of the methoxyl in the hemlock tannin showed resistance towards hydriodic acid, and we therefore re-heated the Perkin-Zeisel apparatus on the following day after the methoxy-estimations had been carried out, as described by Herzig (*Monatsh.*, 1905, **25**, 603; 1908, **29**, 263) during his investigation of ellagic acid. We were thus able to observe an increase in the methoxy-content which, however, could be accounted for by the formation of a

Purified hemlock tannin is a pink, amorphous powder which does not melt when heated above 300° , but begins to decompose at about $260-275^{\circ}$. It is soluble in alcohol, acetone, ethyl acetate, or water, in which it forms deep red solutions. When hydrolysed according to Fischer and Freudenberg's method (*Ber.*, 1912, **45**, 915) for the estimation of sugar in gallotannin, it was found that hemlock tannin does not contain any kind of sugar. With iron chloride it gives a deep green coloration, especially in alcoholic solution. Hemlock tannin is precipitated by gelatin or alkaloids, and is quantitatively absorbed by caseinogen (compare Körner and Nierenstein, *Chem. Zeit.*, 1911, **36**, 31; Nierenstein, *Annalen*, 1912, **388**, 224; Spiers, *J. Agric. Sci.*, 1919, **6**, 77).

Alkali Hydrolysis of Hemlock Tannin.

(1) *Alcoholic Potassium Hydroxide*.—The only definite fission product obtained by this method was protocathechuic acid, crystallising from water in small needles melting at $191-194^{\circ}$, carbon dioxide being evolved. When mixed with protocathechuic acid, no depression (m. p. $193-194^{\circ}$) was observed.

(2) *Alcoholic Barium Hydroxide*.—We originally used aqueous barium hydroxide with some success, but later employed the methyl-alcoholic solution (compare Müller, T., 1915, **107**, 874). This hydrolysis yielded protocathechuic acid, 2:3-dihydroxybenzoic acid, and a new substance, $C_{10}H_8O_3$, which was apparently an aldehyde.

The hydrolysis was carried out by heating about 10 grams of hemlock tannin with an excess of methyl-alcoholic barium hydroxide for eight to ten hours under reflux. The alcohol was then removed on the water-bath, and the residue diluted with water and acidified with dilute sulphuric acid. The liquid, and also the barium sulphate precipitate, were extracted several times with ether, and the ethereal solution (solution A) treated with sodium hydrogen carbonate solution saturated with carbon dioxide. The aqueous part thus obtained was acidified and extracted with ether (solution B), and both ethereal solutions were investigated separately.

Ethereal Solution A.—The solution left, on evaporation, a tarry precipitate of silver iodide when hydriodic acid and acetic anhydride are left for twenty-four hours and then heated (Manning and Nierenstein, *Ber.*, 1913, **46**, 3983. Critics of this note (compare G. Goldschmidt, *Ber.*, 1914, **47**, 389; A. G. Perkin and Oesch, T., 1914, **105**, 2352) appear to have overlooked the necessity of allowing the mixture to remain for at least a day before any precipitation of silver iodide can be obtained.

mass, which became solid on rubbing and kneading with light petroleum. The dry solid was then extracted in a Soxhlet apparatus with benzene, when the greater part of the product dissolved, leaving a tarry residue in the thimble. The benzene was evaporated to dryness, and the residue (about 0.8 gram) crystallised from alcohol and benzene, from which it separated in small, silky plates melting at 125–126°. It is also soluble in alcohol or much benzene or toluene, from which solutions it crystallises in needles (m. p. 125–126°) after strong concentration of the solvents.

Found: C=68.45; H=4.83. M.W.=160, 166.

$C_{10}H_8O_3$ requires C=68.18; H=4.54 per cent. M.W.=176.

With phenylhydrazine it forms a *phenylhydrazone*, which crystallises from glacial acetic acid in dark brown needles melting and decomposing at 191°.

Found: N=17.91, 17.49.

$C_{10}H_8O_2N_2$ requires N=17.27 per cent.

When oxidised on the water-bath with potassium permanganate in alkaline suspension, it yields the *acid*, $C_6H_7O_2 \cdot CO_2H$, which crystallises from water in long, prismatic needles melting at 214–216°, carbon dioxide being evolved.

Found: C=62.42; H=4.60.

$C_{10}H_8O_4$ requires C=62.50; H=4.20 per cent.

The *sodium* and *potassium* salts were prepared and crystallised from water.

Found: Na=11.12; K=20.86.

Calculated: Na=10.74; K=20.40 per cent.

Diazomethane yields the *methyl* ester, which crystallises from benzene in silky needles melting at 152–153°.

Found: C=64.24; H=4.82.

$C_{11}H_{10}O_4$ requires C=64.18; H=4.62 per cent.

Ethereal Solution B.—The residue which was left on evaporation of the ether crystallised from water in small needles melting indefinitely between 145° and 168°, although the product was recrystallised several times from that solvent. The only definite colour reactions obtained were those of protocatechuic acid, and the analytical data also agreed* for a dihydroxybenzoic acid. (Found: C=54.12; H=4.22. $C_7H_6O_4$ requires C=54.52; H=3.94 per cent.) Attempts were made to separate the mixture by fractional crystallisation, but no fraction of a definite melting point was obtained. The product when heated with soda-lime only gave, so far as could be ascertained, catechol (small needles from

benzene, m. p. 102—103°, from which we concluded that the mixture consisted probably of protocatechuic acid (m. p. 198—199°) and 2:3-dihydroxybenzoic acid (m. p. 204°) (compare Praxmarer, *Monatsh.*, 1906, **27**, 1199; also abstract of this paper, A., 1907, **92**, i, 216, where the melting point is wrongly given as 240°). The product was therefore treated in ethereal solution with diazomethane and converted into the methyl esters of veratric acid (m. p. 59—60°) and 2:3-dimethoxybenzoic acid (m. p. 57—58°) (compare Praxmarer, *loc. cit.*), and the mixture fractionated under diminished pressure. Sixteen grams of the methyl esters gave the following fractions, which crystallised from benzene on subsequent solidification:

Fraction I.—1.84 Grams, b. p. 124—127°/10—11 mm., m. p. 47—53°.

Fraction II.—1.26 Grams., b. p. 124—126°/10—12 mm., m. p. 52—54°.

Fraction III.—4.47 Grams, b. p. 125—127°/10—12 mm., m. p. 55—56°.

Fraction IV.—2.12 Grams, b. p. 126—129°/10—11 mm., m. p. 58—59°.

Each fraction was hydrolysed on the water-bath with alkali, and the free methoxy-acids were crystallised from dilute alcohol. These fractions melted as follows:

Fraction I.—M. p. 162—168°.

Fraction II.—M. p. 178—180°. Mixed m. p. with veratric acid, 178—180°; mixed m. p. with 2:3-methoxybenzoic acid, 158—164°.

Fraction III.—M. p. 176—183°. Mixed m. p. with veratric acid, 164—171°; mixed m. p. with 2:3-dimethoxybenzoic acid, 172—178°.

Fraction IV.—M. p. 184—186°. Mixed m. p. with veratric acid, 168—174°; mixed m. p. with 2:3-dimethoxybenzoic acid, m. p. 183—185°.

The melting point of veratric acid is given as 181° (compare Freund and Niederhofheim, *Ber.*, 1896, **29**, 858; Kostanecki and Tambor, *Ber.*, 1907, **39**, 4022). There is, however, no reference to 2:3-dimethoxybenzoic acid. This was therefore prepared by the action of diazomethane on 2:3-dihydroxybenzoic acid prepared according to Praxmarer's method (*loc. cit.*); the ester was subsequently hydrolysed and the methoxy-acid crystallised from dilute alcohol, from which it separated in needles melting at 187—188°, carbon dioxide being evolved. (Found: C=59.14; H=5.72. $C_9H_{10}O_4$ requires C=59.31; H=5.54 per cent.)

From the above data, it is probable that fraction II consisted mainly of veratric acid (Found: C=59.12; H=5.78. Calc.: C=59.31; H=5.54 per cent.), whereas fraction IV consisted of 2:3-dimethoxybenzoic acid (Found: C=58.92; H=5.46. Calc.: C=59.31; H=5.54 per cent.), from which we conclude that protocatechuic and 2:3-dihydroxybenzoic acids are formed during the hydrolysis of hemlock tannin.

Methylated Hemlock Tannin.

Hemlock tannin was methylated with diazomethane in ethereal suspensions, fractions IV, V, and VI only being used for the methylation. The dry tannin was suspended in ether, as used in the Grignard reaction (compare Clibbens and Nierenstein, T., 1915, 107, 1491), and an excess of diazomethane allowed to act on it for about twelve hours. In the case of fraction IV there was always a residue, after methylation, insoluble in ether [similar observations were made by Herzig (*Monatsh.*, 1912, 33, 843), and Fischer and Freudenberg (*Ber.*, 1912, 45, 2723), during the methylation of gallotannin with diazomethane]. Fraction V also left a small residue, but fraction VI on methylation dissolved completely in ether.

The ethereal solution was filtered and the ether removed under diminished pressure. The residue was purified by dissolving in a little alcohol and pouring into water. It frequently happened that the methylated product did not separate out readily, in which case the liquid was shaken vigorously to coagulate the precipitate and allowed to remain for a time. The precipitate was then collected, carefully washed, and dried in a desiccator.

Methylated hemlock tannin obtained in this way after several precipitations was a white, amorphous product with a more or less distinctly yellow tint; it was readily soluble in alcohol, ether, acetone, benzene, carbon tetrachloride, or *s*-tetrachloroethane, but insoluble in light petroleum. The product had no definite melting point; it sintered at 74–79° and melted at 134–141°.

Found: C=65.69, 65.25, 64.82, 65.12; H=5.58, 5.46, 5.82, 5.27; OMe=26.48, 25.65, 25.84 per cent. M.W. (in chloroform)=620, 561, 552, 574.

The methoxy-estimations were carried out in a Zeisel-Perkin apparatus, acetic anhydride being added. If the latter was replaced by phenol (compare Weishut, *Monatsh.*, 1913, 33, 1165), the same result was obtained (OMe=25.76 per cent.). In view of the experiences of W. Richter (*Diss.*, Erlangen, 1902, 44), who found that eutannin is more fully methylated with diazomethane

in an acetone solution than in an ethereal one, we also used the former as a solvent, without, however, increasing the methoxy-content. (Found: OMe=25.89 per cent.). For similar reasons, we also used methyl alcohol as a solvent (compare Geake and Nierenstein, *Biochem. J.*, 1914, **8**, 292), the result being the same (Found: OMe=25.43 per cent.).

Methylated hemlock tannin was found to be optically active: $[\alpha]_D^{25}$ -41° (in chloroform), -24.7° (in *s*-tetrachloroethane), 50.1° (in alcohol), and -16.9° (in acetone).

Alkali Hydrolysis of Methylated Hemlock Tannin.

Methylated hemlock tannin (about 5—10 grams) was hydrolysed by boiling with a 10 per cent. solution of alcoholic potassium hydroxide for about three hours. The alcohol was then evaporated, and the residue extracted with boiling water and filtered from any incompletely hydrolysed or tarry substance. On acidifying with dilute sulphuric acid, the filtrate gave a bulky precipitate (precipitate A), which was collected, washed, and dried in a desiccator. The filtrate was extracted with ether several times, and the ethereal extract treated with a 5 per cent. solution of sodium hydrogen carbonate saturated with carbon dioxide. Nothing was found to remain in the ether. The sodium hydrogen carbonate solution was acidified with dilute sulphuric acid and extracted with ether. On evaporation of the ether, a residue was obtained which was crystallised several times from water with the addition of animal charcoal, when small crystals were obtained melting at 208°. They proved to be vanillic acid, and gave no depression of the melting point when mixed with vanillic acid. (Found: C=57.02; H=5.08. Calc.: C=57.11; H=4.81 per cent.)

Precipitate A.—The product was purified by dissolving several times in alcohol and precipitating with water.

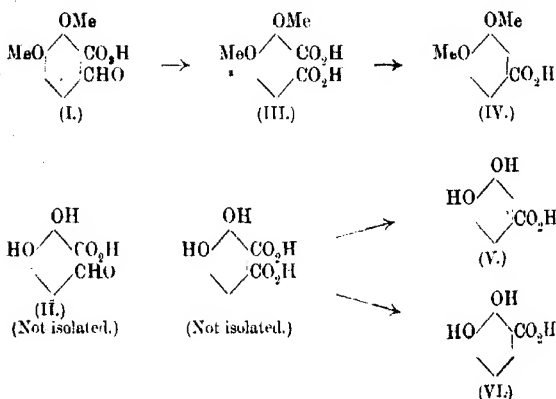
Found: C=67.14, 66.83; H=6.49, 6.22; OMe=28.18 per cent.

When oxidised with potassium permanganate in alkaline solution, hemipinic acid was produced. The following method of oxidation gave the best results. 1.5 Grams of the substance were heated on a water-bath for six to eight hours with 75 c.c. of 2*N*-potassium hydroxide and 3 grams of potassium permanganate dissolved in about 50 c.c. of water, which were added in two portions. The solution was acidified, filtered, and extracted with ether. The residue left on evaporation crystallised from water in small needles, which melted when slowly heated at 170—173° (compare Nierenstein, *Annalen*, 1913, **396**, 198; Pschorr and

Samuleanu, *Ber.*, 1899, **32**, 3411), which melting point was not depressed when mixed with hemipinic acid prepared from opianic acid. (Found: C=53.33; H=5.09. Calc.: C=53.07; H=4.47 per cent.)

Mild hydrolysis of precipitate A furnished opianic acid, which was obtained on warming 2 grams of the substance with 20 c.c. of 2*N*-alcoholic potassium hydroxide for several hours on the water-bath under reflux at a temperature not higher than 60°. The alcohol was evaporated, the residue acidified, and extracted with ether. The ethereal extract was shaken with sodium hydrogen carbonate solution saturated with carbon dioxide, and the aqueous part, after acidification with dilute sulphuric acid, extracted with ether. The carefully dried residue which was left on evaporation of the ether deposited, from benzene, thin, prismatic needles melting at 147—149°. When mixed with opianic acid, no depression of the melting point was observed. (Found: C=56.82, 56.78; H=5.12, 4.94. Calc.: C=57.11; H=4.81 per cent.) A small amount was converted into the oxime, crystallising in small needles melting at 81°, which is in the vicinity of the melting point 82—83°, as found by W. H. Perkin, jun. (*T.*, 1890, **57**, 1071). There was not enough material for a combustion.

The fact that the methylated hemlock tannin yields opianic acid (I) suggests the possible existence of noropianic acid (II) in hemlock tannin, which probably explains the formation of hemipinic acid (III) and veratric acid (IV) from methylated hemlock tannin and protocatechuic acid (V) and 2:3-dihydroxybenzoic acid (VI) from hemlock tannin:



In conclusion, we wish to take this opportunity of expressing our thanks to the Research Fund Committee of the Chemical Society, and to the Colston Society of the University of Bristol, for grants towards this investigation. We also wish to thank Messrs. Davis and Sons, Tanners, Kingston, Canada, for a generous supply of hemlock bark.

BIOCHEMICAL LABORATORY,
CHEMICAL DEPARTMENT,
UNIVERSITY OF BRISTOL.

[Received, May 6th, 1919.]

LV.—*The Formation of Diazoamino-compounds from β -Naphthylamine.*

By GEORGE MARSHALL NORMAN.

DURING the preparation of some diazoamino-compounds involving the action of diazotised β -naphthylamine on amines of the benzene series, it was noticed that, in the case of *o*-toluidine, the product was a tarry substance which, on keeping, became a dark red solid and consisted of *o*-tolueneazo- β -naphthylamine (Norman, T., 1912, 101, 1914).

A search has been made for other cases of this result, and as both *m*- and *p*-toluidine gave diazoamino-compounds, *o*-substituted amines have been selected for the purpose. However, a substituent in the *o*-position, even a methyl radicle, is not the only condition necessary, for, although *m*-4-xylydine gave *m*-xylene-4-azo- β -naphthylamine, *p*-xylydine gave a diazoamino-compound, a result also obtained with *o*-chloroaniline, 3-bromo-*p*-toluidine, and 5-bromo-*o*-toluidine. Under the same conditions, diazotised β -naphthylamine does not appreciably react with 3-nitro-*p*-toluidine or 5-nitro-*o*-toluidine, even on keeping for several hours. The same difficulty was encountered in the case of *s*-trichloroaniline.

The diazoamino-compounds obtained pass quite readily into the isomeric aminoazo-compounds on heating with the contained benzene base and its hydrochloride. This can be explained by the occurrence of an intramolecular change or by a preliminary decomposition into a diazonium salt and β -naphthylamine, with subsequent recombination to form the azo-compound, and this is supported by the formation of μ -tolueneazo- β -naphthylamine on heating diazoamino-*p*-toluene with *p*-toluidine hydrochloride and β -naphthylamine in molecular proportions and excess of *p*-toluidine.

The experiments of Meldola and Streatfeild (T., 1887, **51**, 434) showed that the action of aqueous acids is to decompose mixed diazoamino-compounds into four products, the bases and the corresponding diazonium salts in molecular proportions, but under the conditions of the present experiments the only aminoazo-compound produced is derived from the diazotised benzenoid base and β -naphthylamine in practically quantitative yield. The decomposition into four products evidently does not occur, or one would expect to find β -naphthaleneazo- β -naphthylamine among the products, unless, indeed, β -naphthalenediazonium chloride in the presence of the benzene base is converted into a substituted benzenediazonium chloride.

When the diazoamino-compounds are heated with β -naphthol, either β -naphthylamine or the benzene base is eliminated, and the resulting hydroxyazo-compound is not a mixture in the cases examined. Thus, the diazoamino-compound obtained from 5-bromo-*o*-toluidine gave 5-bromo-*o*-tolueneazo- β -naphthol and eliminated β -naphthylamine, but the compounds from *o*-chloroaniline, 3-bromo-*p*-toluidine, and *p*-xylydine gave β -naphthaleneazo- β -naphthol and eliminated the benzenoid base. Probably this can be best explained by the formation of an unstable intermediate compound, which undergoes decomposition with the elimination of one of the bases present, the mode of decomposition depending on the nature and position of the substituent radicles.

EXPERIMENTAL.

m-Xylene-4-azo- β -naphthylamine, $C_6H_3(CH_3)_2 \cdot N_2 \cdot C_{10}H_7 \cdot NH_2$.

This compound crystallises from methylated spirit in orange-red plates melting at 126° :

0.1345 gave 18 c.c. N_2 (moist) at 16° and 750 mm. $N = 15.4$.

$C_{15}H_{17}N_3$ requires $N = 15.27$ per cent.

The *acetyl* derivative crystallises from ethyl acetate in small, orange-red needles melting at 142° :

0.1235 gave 13.9 c.c. N_2 (moist) at 15° and 752 mm. $N = 13.1$.

$C_{20}H_{19}ON_3$ requires $N = 13.25$ per cent.

The *benzoyl* derivative crystallises from ethyl acetate in bright red needles melting at 145° :

0.1142 gave 11.2 c.c. N_2 (moist) at 17° and 756 mm. $N = 11.3$.

$C_{26}H_{21}ON_3$ requires $N = 11.08$ per cent.

Action of β -Naphthalenediazonium Chloride on m-4-Xylidine.

On the addition of sodium acetate to the cold solution, a brown solid separated which became tarry, and, on keeping, solidified to a red solid, which was identified as *m*-xylene-4-azo- β -naphthylamine.

Reduction of m-Xylene-4-azo- β -naphthylamine.

In order to establish beyond doubt the constitution of this compound, it was reduced with zinc dust in acetic acid solution. Acetic anhydride was then added, and the subsequent addition of a little water caused the separation of a solid, which was identified as diacetyl-1:2-naphthylenediamine, whilst from the mother liquor aceto-*m*-4-xylidide was obtained.

Action of Nitrous Acid on m-Xylene-4-azo- β -naphthylamine.

Meldola and East's method (T., 1888, **53**, 465) gave a tarry solid, which was boiled with alcoholic potassium hydroxide. The product was identified as *m*-xylene-4-azo- β -naphthol (m. p. 166°).

o-Chlorobenzeneazo- β -naphthylamine, $C_6H_4Cl \cdot N_2 \cdot C_{10}H_6 \cdot NH_2$.

This compound crystallises from benzene in red needles melting at 151°:

0.1520 gave 19.5 c.c. N_2 (moist) at 16° and 748 mm. $N=14.71$.

$C_{16}H_{12}N_3Cl$ requires $N=14.93$ per cent.

The *acetyl* derivative crystallises from ethyl acetate in orange-red, silky needles melting at 153°:

0.1324 gave 0.5940 AgCl. $Cl=11.1$.

$C_{18}H_{14}ON_3Cl$ requires $Cl=10.97$ per cent.

The *benzoyl* derivative crystallises from glacial acetic acid in orange needles melting at 167°:

0.1841 gave 0.6955 AgCl. $Cl=9.35$.

$C_{23}H_{16}ON_3Cl$ requires $Cl=9.2$ per cent.

 β -Naphthalenediazoamino-o-chlorobenzene, $C_6H_4Cl \cdot N_3H \cdot C_{10}H_7$.

This compound crystallises from toluene in pale brown, minute needles melting at 100°. When heated with *o*-chloroaniline and its hydrochloride at 60°, it changes readily into the isomeric amino-azo-compound, and when heated with β -naphthol it gives β -naphthaleneazo- β -naphthol and *o*-chloroaniline:

0.1231 gave 15.9 c.c. N_2 (moist) at 17° and 750 mm. $N = 14.8$.
 $C_{16}H_{12}N_3Cl$ requires $N = 14.93$ per cent.

3-Bromo-p-tolueneazo-β-naphthylamine, $C_6H_5MeBr \cdot N_2 \cdot C_{10}H_6 \cdot NH_2$.

This compound crystallises from methylated spirit in glistening, dark red plates melting at 172° :

0.1461 gave 16.0 c.c. N_2 (moist) at 18° and 752 mm. $N = 12.48$.
 $C_{17}H_{14}N_3Br$ requires $N = 12.35$ per cent.

The *acetyl* derivative crystallises from glacial acetic acid in small, yellow needles melting at 168° :

0.1324 gave 0.6459 AgBr. $Br = 20.76$.
 $C_{19}H_{16}ON_3Br$ requires $Br = 20.94$ per cent.

The *benzoyl* derivative crystallises from ethyl acetate in orange-red needles melting at 186° :

0.1448 gave 0.6090 AgBr. $Br = 17.89$.
 $C_{21}H_{18}ON_3Br$ requires $Br = 18.02$ per cent.

4-β-Naphthalenediazoamino-3-bromotoluene,
 $C_6H_5MeBr \cdot N_3H \cdot C_{10}H_7$.

This compound crystallises from methylated spirit in pale brown prisms melting at 104° . On heating with 3-bromo-*p*-toluidine and its hydrochloride at 60° , it passes readily into the isomeric amino-azo-compound, and when heated with β -naphthol eliminates 3-bromo-*p*-toluidine and gives 3-bromo-*p*-tolueneazo- β -naphthol, which crystallises from benzene in red needles melting at 169° :

0.23 gave 24 c.c. N_2 (moist) at 14° and 752 mm. $N = 12.14$.
 $C_{17}H_{14}N_3Br$ requires $N = 12.35$ per cent.

5-Bromo-o-tolueneazo-α-naphthylamine,
 $C_6H_5MeBr \cdot N_2 \cdot C_{10}H_6 \cdot NH_2$.

This compound crystallises from methylated spirit in small, red plates melting at 152° :

0.1542 gave 16.6 c.c. N_2 (moist) at 15° and 754 mm. $N = 12.52$.
 $C_{17}H_{14}N_3Br$ requires $N = 12.35$ per cent.

The *acetyl* derivative crystallises from ethyl acetate in orange-red, feathery needles melting at 189° :

0.1643 gave 0.8115 AgBr. $Br = 21.02$.
 $C_{19}H_{16}ON_3Br$ requires $Br = 20.94$ per cent.

The *benzoyl* derivative crystallises from ethyl acetate in pale orange, feathery needles melting at 179° .

0.1862 gave 0.7859 AgBr. Br = 17.96.

$C_{24}H_{18}ON_3Br$ requires Br = 18.02 per cent.

2- β -Naphthalenediazoamino-5-bromotoluene,
 $C_6H_3MeBr \cdot N_3H \cdot C_{10}H_7$.

This compound crystallises from toluene in small, red needles melting at 113° . When heated with 5-bromo-*o*-toluidine and its hydrochloride at 65° , it passes into the isomeric aminoazo-compound, and when heated with β -naphthol it eliminates β -naphthylamine and yields 5-bromo-*o*-tolueneazo- β -naphthol, which crystallises from benzene in red plates melting at 174° .

0.1459 gave 16 c.c. N_2 (moist) at 19° and 749 mm. N = 12.42.

$C_{17}H_{14}N_3Br$ requires N = 12.35 per cent.

p-Xyleneazo- β -naphthylamine, $C_6H_3Me_2 \cdot N_2 \cdot C_{10}H_6 \cdot NH_2$.

This compound crystallises from methylated spirit in brilliant orange-red needles melting at 119° .

0.1421 gave 18.6 c.c. N_2 (moist) at 17° and 754 mm. N = 15.07.

$C_{18}H_{17}N_3$ requires N = 15.27 per cent.

The *acetyl* derivative crystallises from ethyl acetate in dark red needles melting at 167° .

0.1239 gave 14.2 c.c. N_2 (moist) at 15° and 750 mm. N = 13.24.

$C_{20}H_{19}ON_3$ requires N = 13.25 per cent.

The *benzoyl* derivative crystallises from ethyl acetate in orange-red, feathery needles melting at 148° .

0.1761 gave 16.6 c.c. N_2 (moist) at 15° and 750 mm. N = 10.9.

$C_{25}H_{21}ON_3$ requires N = 11.08 per cent.

2- β -Naphthalenediazoamino-p-xylene, $C_6H_3Me_2 \cdot N_3H \cdot C_{10}H_7$.

This compound crystallises from benzene in brownish-red crystals melting somewhat indefinitely at 120° . On heating with *p*-xylydine and its hydrochloride, a small quantity of a yellow solid melting at 124° , and containing 11.7 per cent. of nitrogen, was obtained, but it was not further identified. On heating with β -naphthol, it gives β -naphthaleneazo- β -naphthol and *p*-xylydine.

0.1213 gave 15.9 c.c. N_2 (moist) at 17° and 754 mm. N = 15.09.

$C_{18}H_{17}N_3$ requires N = 15.27 per cent.

3-Nitro-p-tolueneazo-β-naphthylamine,
 $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{N}_2 \cdot \text{C}_{10}\text{H}_7\text{NH}_2$.

This compound crystallises from toluene in dark bronze needles melting at 224°:

0.1133 gave 18 c.c. N_2 (moist) at 18° and 753 mm. $\text{N} = 18.18$.
 $\text{C}_{17}\text{H}_{14}\text{O}_2\text{N}_4$ requires $\text{N} = 18.3$ per cent.

The *acetyl* derivative crystallises from ethyl acetate or toluene in small, red needles melting at 200°:

0.1441 gave 20.2 c.c. N_2 (moist) at 19° and 753 mm. $\text{N} = 15.95$.
 $\text{C}_{19}\text{H}_{16}\text{O}_3\text{N}_4$ requires $\text{N} = 16.09$ per cent.

The *benzoyl* derivative crystallises from ethyl acetate in red needles melting at 158°:

0.1137 gave 13.7 c.c. N_2 (moist) at 16° and 750 mm. $\text{N} = 13.86$.
 $\text{C}_{24}\text{H}_{18}\text{O}_3\text{N}_4$ requires $\text{N} = 13.66$ per cent.

5-Nitro-o-tolueneazo-β-naphthylamine,
 $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{N}_2 \cdot \text{C}_{10}\text{H}_7\text{NH}_2$.

This compound crystallises from toluene in dark bronze needles melting at 210°:

0.1239 gave 19.1 c.c. N_2 (moist) at 16° and 758 mm. $\text{N} = 17.93$.
 $\text{C}_{17}\text{H}_{14}\text{O}_2\text{N}_4$ requires $\text{N} = 18.3$ per cent.

The *acetyl* derivative crystallises from toluene in red needles melting at 240°:

0.1361 gave 19.2 c.c. N_2 (moist) at 17° and 754 mm. $\text{N} = 16.24$.
 $\text{C}_{19}\text{H}_{16}\text{O}_3\text{N}_4$ requires $\text{N} = 16.09$ per cent.

The *benzoyl* derivative crystallises from toluene in red needles melting at 197°:

0.1356 gave 16 c.c. N_2 (moist) at 16° and 760 mm. $\text{N} = 13.76$.
 $\text{C}_{24}\text{H}_{18}\text{O}_3\text{N}_4$ requires $\text{N} = 13.66$ per cent.

s-Trichlorobenzeneazo-β-naphthylamine, $\text{C}_6\text{H}_2\text{Cl}_3 \cdot \text{N}_2 \cdot \text{C}_{10}\text{H}_7\text{NH}_2$.

This compound crystallises from benzene in red needles melting at 157°:

0.2135 gave 0.2618 AgCl . $\text{Cl} = 30.26$.
 $\text{C}_{16}\text{H}_{10}\text{N}_3\text{Cl}_3$ requires $\text{Cl} = 30.38$ per cent.

The *acetyl* derivative crystallises from ethyl acetate in reddish-yellow needles melting at 169°:

0.2341 gave 0.2556 AgCl . $\text{Cl} = 27.01$.
 $\text{C}_{18}\text{H}_{12}\text{ON}_3\text{Cl}_3$ requires $\text{Cl} = 27.13$ per cent.

Action of p-Toluidine and its Hydrochloride on Diazoamino-p-toluene in the Presence of β-Naphthylamine.

Molecular quantities of diazoamino-*p*-toluene, *p*-toluidine hydrochloride, and β-naphthylamine were dissolved in *p*-toluidine and heated for twelve hours at 50°. On treatment with hydrochloric acid, a residue was obtained which was crystallised from methylated spirit, and melted at 112°. It was identified as *p*-tolueneazo-β-naphthylamine.

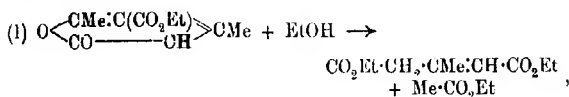
MUNICIPAL TECHNICAL SCHOOL,
BURY, LANCASHIRE.

[Received, May 14th, 1919.]

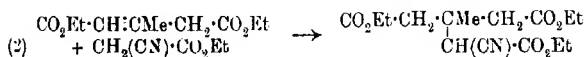
LVI.—*The Chemistry of the Glutaconic Acids.*
Part XI. *The Occurrence of 1 : 3-Addition to the Normal Form.*

By JOCELYN FIELD THORPE.

IN Part IX of this series (T., 1913, 103, 1579) it was shown that the *cis*-labile ester of β-methylglutaconic acid, which can be readily formed by the action of alcoholic sodium ethoxide on ethyl *is*-dehydracetate,



condenses with the sodium compound of ethyl cyanoacetate, giving a 60 per cent. yield of a condensation product in accordance with the equation

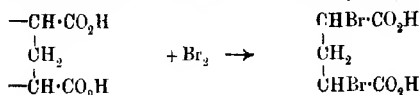


whereas the normal ester, $\text{CO}_2\text{Et} \cdot \dot{\text{C}}\text{H} \cdot \text{CHMe} \cdot \dot{\text{C}}\text{H} \cdot \text{CO}_2\text{Et}$, which can be prepared from the normal acid by etherification, yields no condensation product under the same experimental conditions.

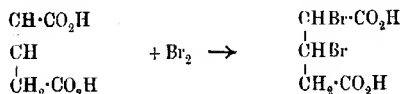
Several other esters of normal acids of the series were subjected to the same reaction, and the failure in each case to obtain a condensation product was regarded as evidence that substances possessing the normal structure which, in accordance with the

views put forward in this series, have constitutions best represented by the general formula $\text{CO}_2\text{R}\cdot\dot{\text{C}}\text{R}\cdot\text{CHR}\cdot\dot{\text{C}}\text{R}\cdot\text{CO}_2\text{R}$ ($\text{R}=\text{H}$ or alkyl), do not form additive products when treated with the usual additive reagents.

The evidence is, however, negative, and during the whole course of these researches on the glutaconic acids, frequent attempts have been made to obtain direct evidence of the structure of the normal forms by inducing them to form additive products in the 1:3-positions. If, for example, bromine could be made to unite with the terminal carbon atoms of the normal system, thus:



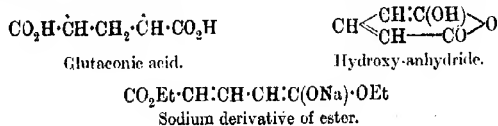
and if the isomeric compound produced from the labile modification were found to be formed in accordance with the scheme:



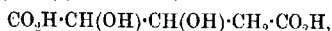
no reasonable doubt would then remain that the formulæ for the glutaconic acids suggested in this series must be a close approximation to the truth.

Unfortunately, the evidence obtained in this way is far from satisfactory. The stable normal acids of the type of β -methylglutaconic acid (the *cis*-acid of Feist, *Annalen*, 1906, **345**, 64, and of Fichter and Schwab, *Annalen*, 1907, **348**, 234, melting at 149°) do not react with the halogen to give any definite additive products, although the *cis*-labile acid (the *trans*-acid of Feist and Fichter, melting at 115 – 116°) readily forms $\alpha\beta$ -dibromo- β -methylglutaric acid, $\text{CO}_2\text{H}\cdot\text{CHBr}\cdot\text{CMeBr}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (m. p. 145°), when treated with bromine in direct sunlight (Fichter and Schwab, *loc. cit.*).

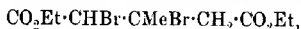
On the other hand, those acids, of which glutaconic acid itself is the best example, the labile forms of which are so unstable as to be incapable of isolation, yet readily pass, either through hydroxyanhydride formation or through the formation of the sodium derivative of the esters, into derivatives of the labile forms (T.



1912, **101**, 863; 1913, **103**, 1757), react with bromine in a curious manner. For example, glutaconic acid readily absorbs the correct amount of bromine, but no one appears to have been able to isolate any definite product from the reaction mixture. Kiliani (*Ber.*, 1885, **18**, 2517) first studied the action of bromine on this acid. He noticed the rapid absorption of the halogen, but, without attempting to isolate the additive product, treated the crude reaction mixture with calcium carbonate and obtained a 10 per cent. yield of $\alpha\beta$ -dihydroxyglutaric acid,



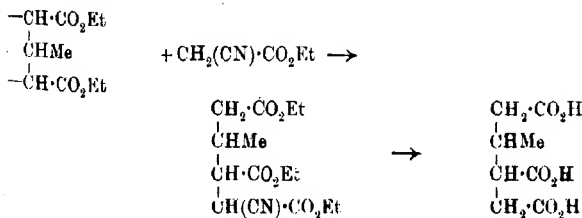
a yield which was subsequently increased to 14 per cent (*Ber.*, 1905, **38**, 3625). Ultimately, Feist (*Ber.*, 1911, **44**, 137) was able to obtain an 80–85 per cent. yield of the dibromo-ester,



by brominating ethyl glutaconate in sunlight.

It is evident, therefore, that the normal acids of this series do not react with bromine in the way one would expect an $\alpha\beta$ -unsaturated acid to react, and that they only form additive products under conditions which favour the transformation of the normal into the labile modifications. The labile acids, on the other hand, are easily converted into $\alpha\beta$ -dibromo-additive products in accordance with the properties of the structures assigned to them.

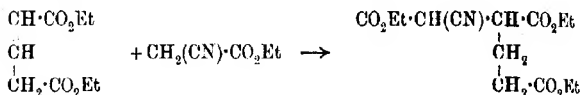
Direct evidence respecting the structure of the normal form can, however, be obtained from a study of the condensation products formed from the normal and labile esters of β -methylglutaconic acid with the sodium compound of ethyl cyanoacetate, for it is now found that whereas the *cis*-labile ester reacts in accordance with equation (2) and gives a yield, which has now been increased to 80 per cent., of the 1:2-additive product, the normal ester can, under special conditions described in the experimental portion, be made to yield a small quantity (approximately 6 per cent.) of a condensation product which, when hydrolysed, is converted into γ -methylbutane- $\alpha\beta\delta$ -tricarboxylic acid, in accordance with the scheme:



an acid which was found by direct comparison to be identical with that prepared by Hope and Perkin (T., 1911, **89**, 762) by the interaction of ethyl bromoacetate and the condensation product of ethyl sodiocyanoacetate with ethyl crotonate.

There can be no question, therefore, that in this reaction addition has been effected in the 1:3-positions, and although the yield is small, the formation of a condensation product having the above composition is direct evidence of the structure of the normal form.

A similar condensation tried with ethyl glutaconate failed to bring about addition in the 1:3-positions, and the product (about 5 per cent. yield) was found to have the structure assigned to it in the previous paper (T., 1913, **103**, 1580). It had therefore been formed in accordance with the scheme:



and it is evident that a small quantity of the normal ester is converted into the labile ester under the experimental conditions used. It is of interest to record at this stage a tendency that has been detected for the *cis*-labile ester to pass into the normal ester when kept. Hitherto, the *cis*-ester has been regarded as a comparatively stable substance. It distils without change, and can be hydrolysed to the corresponding *cis*-acid without conversion into the normal isomeride.

The following facts show, however, that, under certain conditions, the labile ester passes slowly into its normal form. About the middle of 1914, some 600 grams of the *cis*-labile ester had been accumulated for use in the preparation of the "enclosed" ring compound, an account of which is about to be published. It had all been prepared within the previous month, and some of it had already been used in condensation with the sodium compound of ethyl cyanoacetate, and found to give the usual yield of the condensation product. War then broke out, and the ester remaining over was laid aside until January of the present year, that is, for approximately four and a-half years. It happened that the larger quantity of the ester (about 450 grams) was placed in a deep yellow glass bottle, whereas the remaining amount (about 130 grams) was kept in a white glass bottle. Both bottles were placed side by side in a shallow cupboard with glass doors facing a strong north light. In January, 1919, the ester in the white glass bottle was noticed to have become deep brown, and when condensed with the sodium compound of ethyl cyanoacetate was found to give only 20 per

cent. of the usual condensation product. It was therefore distilled and hydrolysed, when the mixture of acids formed was found to consist of 75 per cent. of the normal acid melting at 149° and 25 per cent. of the labile acid melting at $115\text{--}116^{\circ}$. The ester in the yellow bottle, on the other hand, was found to have altered little in colour and to give the usual yield when condensed with ethyl sodiocyanoacetate. After distillation and hydrolysis, it was found to yield the *cis*-acid melting at $115\text{--}116^{\circ}$ in an almost pure form, a small quantity, about 5 per cent. only, of the *trans*-acid being isolated. In order to check these results, a further quantity of the *cis*-labile ester was prepared from ethyl isodehydroacetate and hydrolysed, when the product was found to be the pure *cis*-acid.

It is evident, therefore, that exposure to light for a considerable period of time leads to the partial conversion of the *cis*-labile form into the normal modification.

EXPERIMENTAL.

Condensation of Normal Ethyl β -Methylglutaconate with the Sodium Compound of Ethyl Cyanoacetate.

In the earlier attempt which was made to effect this condensation (T., 1913, 103, 1580), molecular quantities of the ingredients were used, and the mixture was heated on the water-bath for twenty-four hours. As no condensation product could be isolated under these conditions, they were altered in the present instance so as to ensure that a large excess of ethyl cyanoacetate was present throughout the reaction. Forty-two grams of the normal ester, prepared by the etherification of the normal acid, were added to an alcoholic suspension of the sodium compound of ethyl cyanoacetate prepared from 94 grams of the ester and 9.7 grams of sodium dissolved in 110 grams of alcohol, and the mixture was heated for thirty-six hours on the water-bath. Water was then added, and the acidified liquid extracted with ether. Sodium carbonate solution failed to extract any appreciable quantity of acid ester from the ethereal solution, and the latter was therefore dried and freed from ether. The residual oil was then carefully fractionated under diminished pressure, when, besides the two fractions of lower boiling point, consisting of ethyl cyanoacetate and unchanged ethyl β -methylglutaconate, a small fraction (about 4 grams) of high boiling point was isolated.

Ethyl α -cyano- γ -methylbutane- $\alpha\beta\beta$ -tricarboxylate,
 $\text{CH}_2(\text{CO}_2\text{Et})\cdot\text{CHMe}\cdot\text{CH}(\text{CO}_2\text{Et})\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et},$

is a colourless, moderately viscid liquid which boils at 212° , 22 mm.:

0.1932 gave 0.4081 CO_2 and 0.1293 H_2O . $\text{C}=57.66$; $\text{H}=7.41$.

$\text{C}_{15}\text{H}_{28}\text{O}_6\text{N}$ requires $\text{C}=57.5$; $\text{H}=7.4$ per cent.

γ -Methylglutane- $\alpha\beta\delta$ -tricarboxylic Acid,
 $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}.$

Hope and Perkin found it necessary, in order to obtain this acid in a crystalline condition, to hydrolyse their cyano-triethyl ester to the tribasic acid, to etherify this, and, after fractionation, to isolate the potassium salt by the aid of methyl-alcoholic potassium hydroxide. Apparently there is no need to use this method in order to obtain the crystalline acid from the isomeric cyano-triethyl ester described above, because the hydrolysis proceeded rapidly and smoothly through the agency of "50 per cent." aqueous sulphuric acid. Twelve grams of the cyano-triethyl ester were dissolved in an equal volume of concentrated sulphuric acid, care being taken to keep the mixture cool, and allowed to remain at the ordinary temperature for two hours. Water was then added until the solution became slightly turbid, when it was boiled under a reflux condenser for five hours, the alcohol formed during hydrolysis being removed from time to time by detaching the condenser tube from the flask. After the cooled product had been saturated with ammonium sulphate, it was extracted with ether, and the syrupy acid, which rapidly solidified, obtained by evaporating the dried ethereal solution. The crude acid was then purified by treatment with concentrated hydrochloric acid, filtering, and re-crystallising from this solvent. It melted sharply at 154° (Hope and Perkin give $153-154^{\circ}$) (Found: $\text{C}=46.95$; $\text{H}=6.13$. $\text{C}_8\text{H}_{12}\text{O}_6$ requires $\text{C}=47.1$; $\text{H}=5.9$ per cent.).

The acid was found to crystallise in nodular masses, as described by Hope and Perkin, and mixtures of it with Hope and Perkin's acid were found to have the same melting point (154°) as either constituent. It also gave a potassium salt insoluble in methyl-alcoholic potassium hydroxide. Unfortunately, the amount of acid available was insufficient for the purpose of preparing crystalline derivatives, because the anhydro-acid is apparently one of those intractable substances which are very difficult to obtain in a crystalline condition, similar properties being possessed by the aniline and toluidine derivatives of the anhydro-acid. All attempts to prepare these substances in a crystalline condition were

unsuccessful, and it is possible that the same difficulty was encountered by Hope and Perkin, since it will be noticed that no derivatives of this acid are described by them.

The evidence of the mixed melting point is, however, usually accepted as sufficient proof of identity. In the present instance, this is, of course, strengthened by the fact that the only other acid of this formula which could be produced in the reaction, namely, $\beta\beta$ -dimethylpropanetricarboxylic acid, $\text{CMe}(\text{CH}_2\text{CO}_2\text{H})_3$ (T., 1913, **103**, 1583), melts at 172° and readily gives a crystalline anhydro-acid, which can be converted into a crystalline anililide and trianilide.

The Transformation of cis-Labile Ethyl β -Methylglutamate into the Normal Form.

There is little to add to the general description of this change given in the introductory portion. The labile ester contained in the white glass bottle, which had previously given the usual yield of the condensation product with the sodium compound of ethyl cyanoacetate, was found at the end of four and a-half years to give a yield of only 20 per cent. under the same experimental conditions. It was therefore distilled, and was found to have the same boiling point as the original ester. When hydrolysed, it was found, however, that a mixture of acids was obtained, from which an insoluble, crystalline barium salt could be isolated in large quantities when the neutral ammonium salts of the mixed acids were treated with barium chloride solution and boiled. This was collected and converted into the acid, which was found to melt at 149° (Found: C=49.89; H=5.68. $\text{C}_6\text{H}_8\text{O}_4$ requires C=50.0; H=5.6 per cent.).

This acid, which was evidently, therefore, the normal acid, constituted approximately 75 per cent. of the mixture. The labile acid melting at 115 – 116° was isolated in the usual manner from the mother liquors of the barium salt precipitation.

The ester which had been kept in the deep yellow bottle, and had altered little in appearance, was found on conversion into the acids to yield only a small quantity of an insoluble barium salt, from which the acid melting at 149° was isolated. The amount constituted about 5 per cent. of the mixed acids obtained, the remainder being the *cis*-labile acid melting at 115 – 116° , which was isolated from the mother liquors. The original ester was also found to give approximately the normal yield of con-

denensation product with the sodium derivative of ethyl cyanoacetate.

The change was further proved by preparing some fresh *cis*-labile ester from ethyl *isodehydracetate*, when the product was found to yield the pure labile acid on hydrolysis.

THE IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON.

[Received, June 3rd, 1919.]

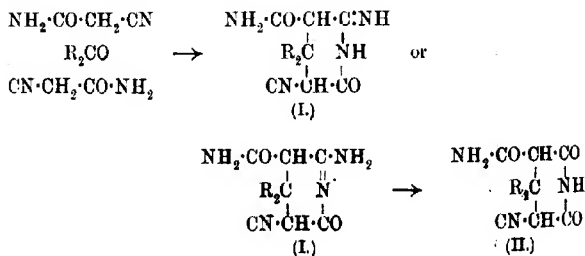
LVII.—*The Formation and Reactions of Imino-compounds. Part XIX. The Chemistry of the Cyanoacetamide and Guareschi Condensations.*

By GEORGE ARMAND ROBERT KON and JOCELYN FIELD THORPE.

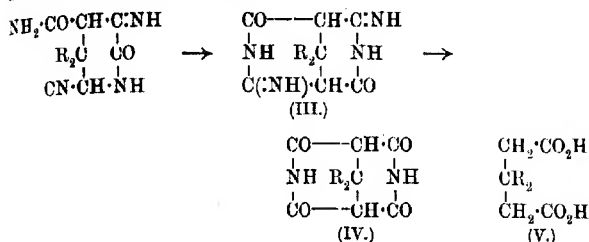
FROM the experiments described in Part XV (T., 1911, **99**, 422) and Part XVIII (T., 1913, **103**, 1586) of this series, it can be concluded that the condensation of cyanoacetamide with ketones in the presence of piperidine yields, to an extent of approximately 95 per cent., products which have the groups attached to the terminal carbon atoms arranged in the *trans*-positions to one another, and that approximately 5 per cent. only of the condensation product has the *cis*-configuration. The proportions vary slightly with the nature of the ketone used and with the temperature at which the condensation is carried out, but is generally of the above order when the reactions are effected at the ordinary temperature.

The following considerations support this conclusion:

(1) The chief product is obtained as a base (I) soluble in dilute mineral acid, which is quickly hydrolysed by the acid to the imide (II) in accordance with the scheme:

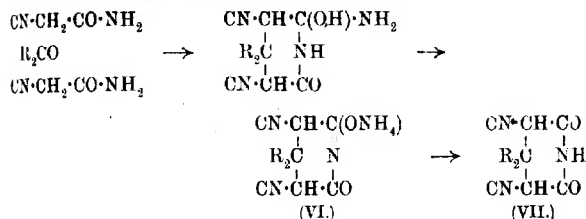


The *trans*-configuration is further proved by the formation of the di-imino-di-imide (III), thus:

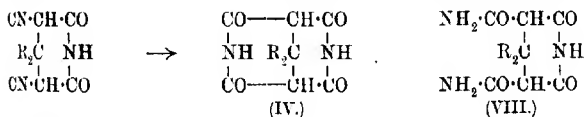


and the general structure of the whole series is shown by the production of the acid (V) from each of these compounds on complete hydrolysis.

(2) A small quantity of condensation product is also obtained which is soluble in alkali, and is evidently present in the condensation mixture as an ammonium salt (VI), since it yields the imide (VII) on treatment with mineral acids:



The *cis*-configuration of this substance follows from the production, with sulphuric acid, of a di-imide identical with (IV) or the

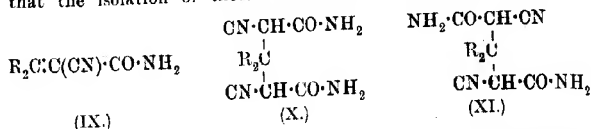


corresponding diamide (VIII), and the general structure from the fact that it yields the acid (V) on complete hydrolysis.

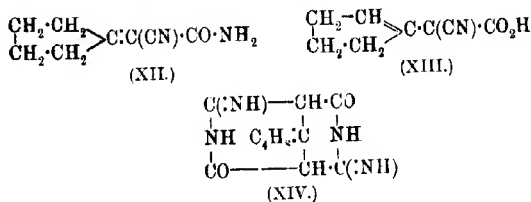
On the other hand, it is certain that when substances of these types are prepared by the action of alcoholic ammonia on a mixture of the ketone and ethyl cyanoacetate (Guarreschi's method), there appears to be no tendency for the condensation product to assume the *trans*-structure, and the compounds prepared in this way have the *cis*-configuration, being, in fact, identical with the

substances of types (VI) and (VII) above. Guareschi's reactions are usually carried out at 40°, and if the cyanoacetamide condensations are effected at a similar temperature, the quantity of the *cis*-product is increased, but the fact that no trace of a *trans*-condensation product can be isolated under Guareschi's conditions shows that direction into *cis* or *trans* is dependent on the reaction and is not appreciably affected by the temperature.

It is evident that the cyanoacetamide condensation can also yield three other products, namely, the initial condensation product (IX) and the open-chain compounds (X) and (XI), and that the isolation of these substances must depend (1) on the

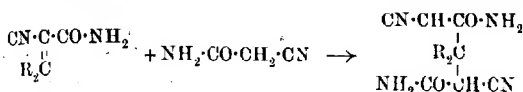


tendency for the double compound to form, and (2) on the tendency which exists for the six-membered ring to be produced. As regards (X) and (XI), we have not been able to isolate any trace of them in ketone condensations, although, as will be shown in a subsequent paper, they are the chief products when certain aldehydes are used in place of ketones. The formation of (IX) has been noticed in one case, which is described in this paper, and its production and reactions clearly show the general mechanism of these condensations. It was found, for example, that when *cyclopentanone* is condensed with cyanoacetamide under conditions which usually yield the cyclic imino-compound (type I), the product is the unsaturated amide (XII).

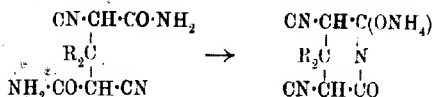


It is true that this amide yields, on treatment with nitrous acid, α -cyano- Δ^1 -cyclopenteneacetic acid (XIII), identical with the compound obtained by Harding and Haworth (T., 1910, **97**, 486), but the fact that it readily condenses with more cyanoacetamide to form the di-imino-compound (XIV) is, we think, proof that it must have the formula (XII). Its precipitation in the present instance is due entirely to its insolubility in the aqueous medium

used, because, if sufficient alcohol is employed, the reaction pursues a normal course with the direct production of the di-imino-derivative (XIV). The production of this intermediate product is, however, of interest, since it is probable that in all cases of this kind the initial condensation leads to the formation of the unsaturated derivative, which then reacts further with cyanoacetamide, forming the glutaric derivative. If this is the correct explanation, it is easy to understand the difference between the cyanoacetamide condensation and the Guareschi reaction, because, in the former case, it is to be anticipated that the addition of cyanoacetamide will lead to the more stable *trans*-configuration,



whereas in Guareschi's reaction the presence of excess of ammonia causes the production of the *cis*-derivative, owing to the tendency for the compound to pass into the ammonium salt,

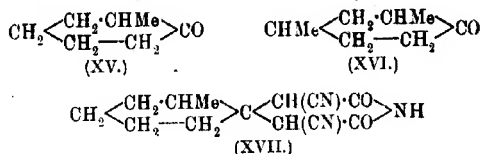


The latter is therefore an "enforced" reaction, and can, as will be shown, be made to yield condensation products in cases where a true catalytic reaction, such as the cyanoacetamide reaction, fails owing to a lack of tendency on the part of the ketone to yield a condensation product. It is found, for example, that the cyanoacetamide reaction can be effected with all ketones having two secondary carbon atoms next to the carbonyl group. If one of these is tertiary, the cyanoacetamide condensation fails, but products can be obtained by the Guareschi method, although in diminished yield. If both carbon atoms are tertiary, both the cyanoacetamide reaction and Guareschi's reaction fail to yield condensation products, and the same is the case if one carbon atom is quaternary, as in camphor and pinacolin.

We have been led to adopt this explanation of the course of the two reactions on account of the results of a series of experiments which have now been carried out on the question of the elimination of an alkyl group from the ortho-position during the condensation of ketones containing such groups with cyanoacetamide.

In Part XVIII (*loc. cit.*) it was noticed that 2-methylcyclohexanone (XV) and 2:4-dimethylcyclohexanone (XVI) gave with cyanoacetamide and piperidine the same condensation products as

those derived from *cyclohexanone* and 4-methyl*cyclohexanone* respectively:



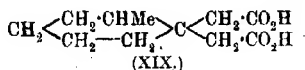
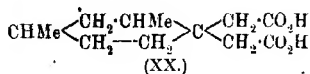
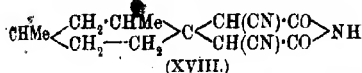
Great care was taken to purify these ketones, and although the yields of the condensation products were small and the reactions very sluggish, their constitutions were unquestionable. It was therefore assumed that the inhibiting effect of the *ortho*-methyl group prevented condensation, but that a certain portion of the ketone eliminated the inhibiting methyl group and yielded the product next lower in the series. At the same time, it was mentioned that Squintani (*Atti R. Accad. Sci. Torino*, 1912—1913, 48, 675) had prepared from 2-methyl*cyclohexanone* by the Guareschi method a condensation product melting at 210°, to which he assigned the structure XVI. It was also pointed out that the melting point of this substance was very close to that of the corresponding compound from *cyclohexanone*, namely, 211—212°, and it was suggested that in this case also the *ortho*-methyl group had been eliminated.

The whole question has now been re-examined, and the pure *o*-methyl ketones have been regenerated from the carefully purified semicarbazones, with the result that it has been established beyond question that the *ortho*-substituted ketones do not react with cyanoacetamide, but give by the Guareschi method a poor yield of the *ortho*-substituted condensation product.

It follows also that the "pure" *o*-methyl ketones of Messrs. Poulenc contain appreciable quantities of the next lower homologue, which, curiously enough, cannot be detected either by analysis or by the precipitation of the semicarbazones, a fact that can be demonstrated in the following way. The "pure" 2-methyl*cyclohexanone* of Messrs. Poulenc when treated with semicarbazide in slight excess was found to give a semicarbazone melting at 183—184°, in the crude condition, and at 190—191°, the correct melting point of the semicarbazone of 2-methyl*cyclohexanone*, after being once recrystallised from alcohol (the semicarbazone of *cyclohexanone* melts at 163°). A mixture of pure *cyclohexanone* (15 per cent.) and pure 2-methyl*cyclohexanone* (85 per cent.) was then made up, when it was found that a semicarbazone of the same melting point (183—184°) as that derived from the Poulenc

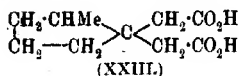
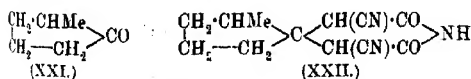
ketone was obtained. As a matter of fact, the presence of *cyclohexanone* could not be detected at all in this mixture. In the same way, the pure semicarbazone of 2:4-dimethyl*cyclohexanone* (melting at 194°) was precipitated from the "pure" ketone of Messrs. Poulenc, although the presence in it of at least 10 per cent. of 4-methyl*cyclohexanone* is clearly indicated by the experiments described in this paper.

Messrs. Poulenc informed us that this ketone must be free from 4-*cyclohexanone*, because it is prepared by the Sabatier-Senderens process from *m*-4-xyleneol. It is evident, however, that the ortho-methyl group is eliminated during the Sabatier-Senderens reduction, and not during the cyanoacetamide condensation. It is also evident that Squintani was dealing with a similar mixture of *cyclohexanone* and 2-methyl*cyclohexanone*, since the condensation product (XVII) prepared from the pure ortho-methyl ketone melts at 245°, and not at 210°. The structures of our products (XVII) and (XVIII) follows from the fact that they are completely converted into the acids (XIX) and (XX) on complete hydrolysis.

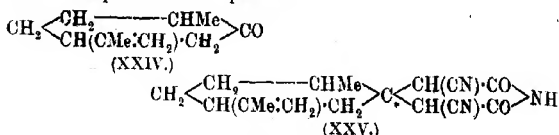


In order still further to emphasise the difference between the two types of reactions, we have investigated several other ketones having one tertiary carbon atom next to the carbonyl group. These compounds do not form condensation products with cyanoacetamide, but condense to a limited extent (the yield is usually about 15–20 per cent.) when subjected to the Guareschi reaction. These results may be summarised as follows.

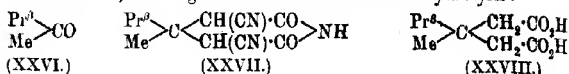
2-Methyl*cyclopentanone* (XXI) yields the condensation product (XXII), which is transformed into the acid (XXIII) on hydrolysis:



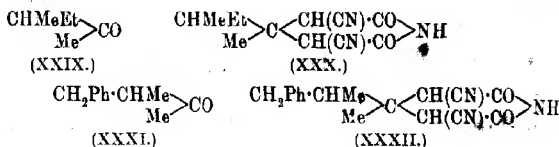
Dihydrocarvone (XXIV) gives a fairly good yield of the condensation product (XXV), which, however, cannot be hydrolysed without deep-seated decomposition.



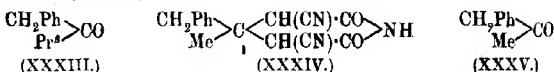
Methyl isopropyl ketone (XXVI) leads to the condensation product XXVII, which gives the acid XXVIII on hydrolysis:



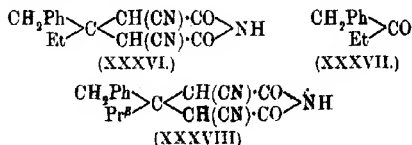
Methyl ψ -butyl ketone (XXIX) is converted into the product XXX, and benzylethyl methyl ketone (XXXI) into the compound XXXII:



The condensation of benzyl isopropyl ketone (XXXIII) with ethyl cyanoacetate and alcoholic ammonia has been described by Guareschi (*Gazzetta*, 1918, **48**, 97), who obtained a condensation product melting at 248°. We have repeated this condensation with the ketone supplied by Messrs. Poulenc, and have isolated both Guareschi's compound and also another which melts at 214—216°. The former we have identified as the benzylmethyl derivative (XXXIV) which we prepared from benzyl methyl ketone (XXXV):



The latter was found to be identical with the benzylethyl derivative (XXXVI) prepared in a similar manner from pure benzyl ethyl ketone (XXXVII):



It is evident, therefore, that the benzyl isopropyl ketone used by Guareschi and by us contained considerable quantities of benzyl ethyl and benzyl methyl ketones. In order to settle this point, we prepared the pure benzyl isopropyl ketone by distilling a mixture of the calcium salts of phenylacetic and isobutyric acids in accordance with Ludlam's method (T., 1902, **81**, 1185). The purity of the ketone was controlled by the formation of the semicarbazone, which we found to melt at 138–139°, in agreement with the figure found by Blaise (*Compt. rend.*, 1901, **132**, 480), and not at 126°, the number given by Senderens (*Compt. rend.*, 1910, **150**, 1138).

When condensed with ethyl cyanoacetate by the Guareschi method, no trace of the condensation product (XXXVIII) could be isolated, and it would appear, therefore, that the occurrence of these lower homologues in commercial benzyl isopropyl ketone is another example of the elimination of ortho-alkyl groups.

Some of the acids formed from these condensation products on hydrolysis appear to be abnormal, and a description of them is therefore reserved for a future communication.

EXPERIMENTAL.

The condensation of ketones with cyanoacetamide was carried out in the manner already described (T., 1911, **99**, 424). For the condensations with ethyl cyanoacetate, Guareschi's instructions were, in the main, followed. The ketone (one molecular proportion) was mixed with ethyl cyanoacetate (two molecular proportions), and a little more than three molecular proportions of ammonia, dissolved in absolute methyl or ethyl alcohol, added to the mixture. The solution assumed a yellow or orange colour and became warm. It was kept at 40° for forty-eight hours, by which time the ammonium salt of the dicyanopiperidine derivative had separated; in many instances, some cyanoacetamide was precipitated at the same time. In all cases, sufficient water was added to dissolve the salt, the solution extracted with ether to remove unchanged ketone, and the extracted solution acidified, when the dicyanopiperidine was precipitated, usually in several crops. All the compounds of this type were found to be colourless and to crystallise remarkably well.

2-Methylcyclohexanone (XV, p. 690).

This ketone, when carefully purified by regenerationg it from the pure semicarbazone, does not condense with cyanoacetamide, the latter being recovered unchanged.

With ethyl cyanoacetate and alcoholic ammonia, the commercial preparations of the ketone give mixtures containing varying quantities of two compounds, one melting at 207° and the other at 245°. They can be separated by a tedious process of fractional crystallisation from 50 per cent. aqueous alcohol; the compound of higher melting point is the less soluble and crystallises out first, but mixtures of various melting points, ranging from 190° to 210°, are obtained intermediately, and this probably accounts for the results obtained by Squintani (see p. 690).

The compound melting at 207° was identified by direct comparison and by analysis (Found: C=62.28; H=5.79. $C_{12}H_{13}O_2N_3$ requires C=62.3; H=5.6 per cent.) as the ω -imide of $\alpha\alpha'$ -dicyanocyclohexane-1:1-diacetic acid, $C_6H_{10} \cdot C \begin{smallmatrix} \text{CH(CN)CO} \\ \text{CH(CN)CO} \end{smallmatrix} > NH$ (compare Thorpe and Wood, T., 1913, 103, 1592). On hydrolysis with 60 per cent. sulphuric acid, it yielded cyclohexane-1:1-diacetic acid, melting at 181°, which was identified by direct comparison with a specimen prepared from cyclohexanone.

The compound melting at 245° is the sole product of the reaction if the ketone used is absolutely pure; the yield is about 3 grams from 11.2 grams of the ketone.

The ω -imide of $\alpha\alpha'$ -dicyano-2-methylcyclohexane-1:1-diacetic acid (XVII, p. 690) crystallises from 50 per cent. aqueous alcohol in glistening plates and melts at 245° with slight decomposition:

0.1016 gave 0.2375 CO_2 and 0.0557 H_2O . C=63.80; H=6.09.

0.1182 „ 17.7 c.c. N_2 at 19° and 766 mm. N=17.34.

$C_{13}H_{15}O_2N_3$ requires C=63.7; H=6.1; N=17.1 per cent.

The ω -imide of $\alpha\alpha'$ -dicarbamyl-2-methylcyclohexane-1:1-diacetic acid, $CH_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{CHMe} \\ \text{CH}_2 - \text{CH}_2 \end{smallmatrix} > C \begin{smallmatrix} \text{CH(CO.NH}_2\text{)CO} \\ \text{CH(CO.NH}_2\text{)CO} \end{smallmatrix} > NH$, is obtained as a microcrystalline precipitate when the above dicyano-derivative is dissolved in ten times its weight of concentrated sulphuric acid and the solution, after keeping for twenty-four hours at the ordinary temperature, is poured into ice-water. It crystallises from absolute alcohol in small plates, which melt and decompose at 275°:

0.1357 gave 0.2735 CO_2 and 0.0828 H_2O . C=54.96; H=6.78.

0.1583 „ 21 c.c. N_2 at 21° and 755 mm. N=14.94.

$C_{13}H_{19}O_4N_3$ requires C=55.5; H=6.8; N=14.9 per cent.

2-Methylcyclohexane-1:1-diacetic acid (XIX, p. 691) is formed in excellent yield when the dicyano-derivative is hydrolysed by 60 per cent. sulphuric acid in accordance with the method described by Thole and Thorpe (T., 1911, 99, 434). It crystallises from dilute alcohol in colourless, iridescent plates, or from benzene,

in which it is sparingly soluble, in prismatic needles. Both forms melt at 148°:

0.1088 gave 0.2462 CO₂ and 0.0816 H₂O. C=61.70; H=8.33.

C₁₁H₁₈O₄ requires C=61.7; H=8.4 per cent.

A normal solution of the neutral ammonium salt of the acid does not give a precipitate with either barium or calcium chlorides, but if more concentrated solutions are used, a copious precipitate of the calcium salt can be obtained on boiling. The *silver* salt is a white, curdy precipitate:

0.1266 gave 0.0634 Ag. Ag=50.05.

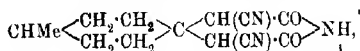
C₁₁H₁₆O₄Ag₂ requires Ag=50.45 per cent.

Neither the anhydride nor the semianilide of this acid could be obtained in a crystalline condition, although the former can be readily prepared as an oil, insoluble in aqueous sodium hydrogen carbonate solution, by treating the acid with hot acetyl chloride.

2:4-Dimethylcyclohexanone (XVI, p. 690).

The pure ketone, regenerated from the semicarbazone, does not condense with cyanoacetamide. Commercial preparations of the ketone readily condense with ethyl cyanoacetate, 12.6 grams of the ketone giving about 3.2 grams of a crude condensation product melting at 205–210°.

On recrystallisation from alcohol, a small amount of a substance crystallising in needles and melting at 213° is obtained from the more soluble portion. This substance was identified as the *ω*-imide of *αα'*-dicyano-4-methylcyclohexane-1:1-diacetic acid,



by direct comparison with a specimen prepared from 4-methylcyclohexanone. The bulk of the product consists of the *ω*-imide of *αα'*-dicyano-2:4-dimethylcyclohexane-1:1-diacetic acid (XVIII, p. 691), which crystallises from alcohol in sparkling plates melting at 236°, not unlike the 2-methyl compound in appearance:

0.1254 gave 0.2970 CO₂ and 0.0751 H₂O. C=64.60; H=6.65.

C₁₄H₁₇O₂N₂ requires C=64.9; H=6.6 per cent.

2:4-Dimethylcyclohexane-1:1-diacetic acid (XX, p. 691) is obtained in good yield when the above dicyano-imide is hydrolysed with 60 per cent. sulphuric acid. It crystallises from water containing a little alcohol in long, prismatic needles melting at 152°, and is very sparingly soluble in benzene:

0.1180 gave 0.2730 CO₂ and 0.0935 H₂O. C=63.10; H=8.80.

• C₁₂H₂₀O₄ requires C=63.2; H=8.8 per cent.

2:4-Dimethylcyclohexane-1:1-diacetic anhydride,



which can be obtained by boiling the acid with acetyl chloride, crystallises from light petroleum (b. p. 60–80°), containing a little benzene, in colourless plates melting at 68.5°:

0.1173 gave 0.2959 CO₂ and 0.0918 H₂O. C=68.77; H=8.70.

C₁₂H₁₈O₃ requires C=68.6; H=8.6 per cent.

The *semianilide*, prepared in the usual manner from a benzene solution of the anhydride and aniline, crystallises from dilute alcohol in glistening laminae melting at 151°:

0.1095 gave 0.2850 CO₂ and 0.0820 H₂O. C=70.97; H=8.13.

C₁₃H₂₃O₃N requires C=71.3; H=8.3 per cent.

Dihydrocarvone (XXIV, p. 692).

The ketone was prepared by the reduction of carvone by zinc dust and sodium hydroxide (Wallach, *Annalen*, 1894, **279**, 377). It does not combine with cyanoacetamide, but condenses fairly readily with ethyl cyanoacetate, the yield of condensation product being about 3 grams from 15.2 grams of the ketone. Care should be taken to remove the unchanged ketone by repeated extraction with ether, otherwise the condensation product is difficult to purify. The sole product of the reaction is the *α-imide* of *αα'-dicyano-2-methyl-5-isopropylidenecyclohexane-1:1-diacetic acid* (XXV, p. 692), which separates from dilute alcohol in clusters of silky needles melting at 198–199°, but sintering and darkening at 197°:

0.1091 gave 0.2698 CO₂ and 0.0667 H₂O. C=67.61; H=6.79.

0.1131 „ 0.2782 CO₂ „ 0.0688 H₂O. C=67.05; H=6.76.

0.0860 „ 10.8 c.c. N₂ at 14.5° and 774.5 mm. N=15.00.

C₁₆H₁₉O₂N₃ requires C=67.4; H=6.7; N=14.7 per cent.

Several attempts were made to hydrolyse this compound to the corresponding non-nitrogenous acid, but a deep-seated decomposition appeared to take place, and we were unable to isolate any crystalline product.

2-Methylcyclopentanone (XXI, p. 691).

This compound was prepared by the hydrolysis of the corresponding carboxylic ester with dilute sulphuric acid, according to

Dieckmann's method (*Annalen*, 1901, **317**, 27). It does not combine with cyanoacetamide, and only gives a very poor yield of condensation product with ethyl cyanoacetate. This consists of the α -imide of $\alpha\alpha'$ -dicyano-2-methylcyclopentane-1:1-diacetic acid (XXII, p. 691), which crystallises from alcohol in glistening plates melting at 237°:

0.0943 gave 0.2109 CO_2 and 0.0484 H_2O . $\text{C}=62.40$; $\text{H}=5.70$.

$\text{C}_{12}\text{H}_{13}\text{O}_2\text{N}_8$ requires $\text{C}=62.3$; $\text{H}=5.6$ per cent.

2-Methylcyclopentane-1:1-diacetic acid (XXIII, p. 691) is obtained from the above dicyano-imide on hydrolysing it with 60 per cent. aqueous sulphuric acid. It crystallises from a mixture of benzene and light petroleum (b. p. 60–80°) in small prisms melting at 112°:

0.1361 gave 0.3010 CO_2 and 0.0998 H_2O . $\text{C}=60.33$; $\text{H}=8.15$.

$\text{C}_{10}\text{H}_{16}\text{O}_4$ requires $\text{C}=60.0$; $\text{H}=8.0$ per cent.

cyclopentanone.

The greater part of the ketone required was prepared by distilling adipic acid with a small quantity of baryta (D.R.-P., Appl. F.33624). The method gives a yield far superior to that obtained by the dry distillation of calcium adipate or by Blanc's method involving the use of acetic anhydride.

Condensation with Cyanoacetamide.—cyclopentanone reacts in this condensation differently from cyclohexanone and its derivatives, owing, presumably, to the greater solubility of the normal condensation product. If the operation is carried out at the ordinary temperature, very little of the imino-compound is formed even if an excess of cyanoacetamide is used. The main product is the amide of α -cyano- Δ^1 -cyclopenteneacetic acid (XII, p. 688), which separates in several crops, usually in rhombohedral crystals. The yield is about 6 grams from 25 grams of cyanoacetamide. A little imino-compound (melting at 287°, see p. 688) also separates in the later stages, and on acidifying the mother liquor, some di-imide (see p. 688) is obtained. The amide possesses a remarkable tendency to crystallise, and can be recrystallised from almost any of the usual solvents. It separates from water in magnificent, long needles, closely resembling phthalic anhydride in appearance. From alcohol, in which it is freely soluble, rhombohedral aggregates are obtained. Similar crystals separate from ethyl acetate, whereas from chloroform, benzene, or light petroleum the compound crystallises in needles. It melts at 134°:

0.1257 gave 0.2949 CO_2 and 0.0756 H_2O . $\text{C}=63.98$; $\text{H}=6.68$
 0.1318 „ 21.5 c.c. N_2 at 13° and 755.5 mm. $\text{N}=18.93$.

$\text{C}_8\text{H}_{10}\text{ON}_2$ requires $\text{C}=64.0$; $\text{H}=6.7$; $\text{N}=18.7$ per cent.

On prolonged boiling with water, and especially dilute alkali, ammonia and some *cyclopentanone* are evolved. On acidifying and extracting with ether, an acid is obtained melting at $130\text{--}131^\circ$. This acid is, however, more conveniently prepared by dissolving the amide (1 gram) in concentrated sulphuric acid (5 c.c.) and slowly adding 6 c.c. of a 20 per cent. sodium nitrite solution to the ice-cold mixture, the reaction being completed by warming on the water-bath for half an hour. On cooling, the solution deposits the acid in thin, felted needles, which, after recrystallisation from a mixture of benzene and light petroleum, melt at $130\text{--}131^\circ$ (Found: $\text{C}=63.70$; $\text{H}=6.18$; $\text{N}=9.57$. $\text{C}_8\text{H}_9\text{O}_2\text{N}$ requires $\text{C}=63.6$; $\text{H}=6.0$; $\text{N}=9.3$ per cent.). The acid is evidently identical with α -cyano- Δ^1 -*cyclopenteneacetic acid* (XII, p. 688) obtained by Harding and Haworth (T., 1910, **97**, 486).

If the condensation of *cyclopentanone* with cyanoacetamide is effected at a higher temperature and care is taken to prevent the precipitation of the amide by adding more alcohol, the reaction proceeds a step further. Thus when 14 grams of cyanoacetamide are dissolved in 50 c.c. of water, 7 c.c. of *cyclopentanone*, 50 c.c. of alcohol, and a few drops of piperidine added, the liquid, after being kept for some time at 37° , deposits a microcrystalline solid, melting and decomposing at 287° , which is completely soluble in dilute mineral acids, and appears to be the ω -di-imino-di-imide of *cyclopentane-1:1-dimalonic acid* (XIV, p. 688). The yield of this substance is, however, poor, and the condensation is not to be recommended for the preparation of the corresponding diacetic acid. Much of the imino-compound remains in solution, and separates on acidifying as the di-imide (see below). The formation of the acid by-product (the dicyano-imide) was not observed.

A similar result is obtained when an alcoholic solution of cyanoacetamide (one molecule) and the amide of α -cyano- Δ^1 -*cyclopenteneacetic acid* (p. 688) is mixed with a few drops of piperidine and allowed to remain at 40° . A small amount of the imino-compound (XIV, p. 688) is deposited first, and, on acidifying, the di-imide separates.

The di-imino-di-imide (XIV, p. 688) is soluble in dilute mineral acids, and separates again if the solution is immediately poured into aqueous sodium acetate, but even then a partial hydrolysis of the imino-groups occurs, and concordant figures could not be obtained on analysis. For the same reason, the platinumchloride could not be prepared uncontaminated with ammonium platin-

chloride. The specimen for analysis was therefore purified by washing, and the analytical figures lead to the formula $C_{11}H_{14}O_2N_4 + \frac{1}{2}H_2O$, but it must be remembered that the compounds of this type burn only with the greatest difficulty:

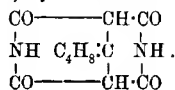
0.1590 gave 0.3177 CO_2 and 0.0920 H_2O . $C=54.50$; $H=6.43$.

0.1125 „ 0.2255 CO_2 „ 0.0647 H_2O . $C=54.67$; $H=6.39$.

0.1535 „ 29.8 c.c. N_2 at 8.5° and 760 mm. $N=23.36$.

$C_{11}H_{14}O_2N_4 + \frac{1}{2}H_2O$ requires $C=54.3$; $H=6.2$; $N=23.1$ per cent.

The ω -Di-imide of cyclopentane-1:1-dimalonic Acid,



This compound is obtained on acidifying the mother liquors from which the di-imino-compound has been filtered off, or by boiling the latter with dilute hydrochloric acid for a short time. It can be produced in a variety of crystalline forms—usually in fern-shaped aggregates of prisms—if allowed to separate slowly from the original liquors. When recrystallised from much alcohol or glacial acetic acid, it is obtained in small, silvery plates which decompose without melting at about 360° :

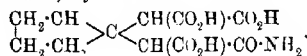
0.1282 gave 0.2608 CO_2 and 0.0616 H_2O . $C=55.48$; $H=5.34$.

0.1814 „ 18.2 c.c. N_2 at 8° and 757 mm. $N=12.03$.

$C_{11}H_{12}O_4N_2$ requires $C=55.9$; $H=5.1$; $N=11.9$ per cent.

The di-imide slowly dissolves in sodium carbonate solution, but is sparingly soluble in all organic solvents.

The Amide of cyclopentane-1:1-dimalonic Acid,



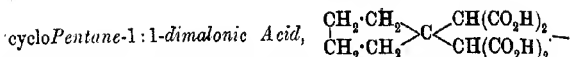
When either the above di-imide or the dicyano-imide (see below) is boiled with a slight excess of 20 per cent. aqueous potassium hydroxide for not longer than three-quarters of an hour, the solution deposits this amido-acid as a crystalline precipitate when acidified. It can be recrystallised from water, and melts with vigorous decomposition at 157° :

0.1636 gave 0.2907 CO_2 and 0.0819 H_2O . $C=48.46$; $H=5.56$.

$C_{11}H_{17}O_7N$ requires $C=48.4$; $H=5.5$ per cent.

0.1647 required 18.20 c.c. of $N/10$ -NaOH for neutralisation.

$C_{11}H_{17}O_7N$ (tribasic) requires 18.10 c.c.

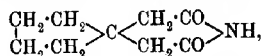


When a solution of the above amido-acid in an excess of 10 per cent. sodium hydroxide solution is boiled until no more ammonia is evolved, and the solution is acidified, the above acid separates. It crystallises from hydrochloric acid in plates, which decompose at 169° into carbon dioxide and cyclopentane-1:1-diacetic acid:

0.1062 gave 0.1872 CO₂ and 0.0510 H₂O. C=48.10; H=5.34.

C₁₁H₁₄O₈ requires C=48.2; H=5.1 per cent.

The imide of cyclopentane-1:1-diacetic acid,

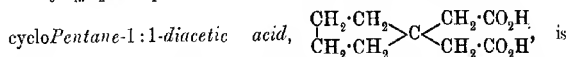


is prepared by heating the amido-tricarboxylic acid at a temperature a few degrees above its melting point until the evolution of carbon dioxide has ceased. It crystallises from water in glistening plates melting at 153°:

0.1139 gave 0.2705 CO₂ and 0.0805 H₂O. C=64.77; H=7.85.

0.1652 „ 13.0 c.c. N₂ at 26.5° and 760.3 mm. N=8.68.

C₉H₁₂O₂N requires C=64.7; H=7.8; N=8.4 per cent.



obtained in excellent yield when either the imino-compound or the di-imide are hydrolysed with sulphuric acid in the usual way. The acid crystallises from water in fern-shaped aggregates of prismatic needles melting at 176—177°. It is sparingly soluble in benzene:

0.1371 gave 0.2910 CO₂ and 0.0920 H₂O. C=57.89; H=7.46.

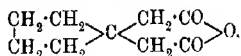
C₉H₁₂O₄ requires C=58.1; H=7.5 per cent.

A normal solution of the neutral ammonium salt of the acid gives no precipitate with barium chloride either in the cold or on boiling. On boiling with normal calcium chloride solution, a white precipitate is formed, which does not redissolve on cooling. The silver salt is a white, curdy precipitate, which slowly darkens on exposure to light:

0.2149 gave 0.1159 Ag. Ag=53.84.

C₉H₁₂O₄Ag₂ requires Ag=54.0 per cent.

cyclopentane-1:1-diacetic anhydride,



is obtained when the acid is boiled with an excess of acetic anhydride or acetyl chloride, and crystallises as the reagent

evaporates. It separates from light petroleum (b. p. 60—80°) containing a little benzene in iridescent laminae melting at 68°:

0.1528 gave 0.3586 CO₂ and 0.0936 H₂O. C=64.02; H=6.81.

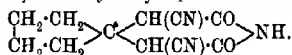
C₉H₁₂O₃ requires C=64.3; H=7.0 per cent.

The *semianilide* is readily obtained on boiling the anhydride and aniline in benzene solution. It crystallises from alcohol in large, colourless laminae melting at 118°:

0.1127 gave 0.2852 CO₂ and 0.0730 H₂O. C=69.03; H=7.20.

C₁₅H₁₉O₃N requires C=69.0; H=7.3 per cent.

The ω-Imide of αα'-Dicyanocyclopentane-1:1-diacetic Acid,



This compound is obtained when *cyclopentanone* is condensed with ethyl cyanoacetate in the presence of alcoholic ammonia, the yield being about 50 per cent. of the theoretical. As a good yield of *cyclopentane-1:1-diacetic acid* can be easily obtained from the dicyano-imide on hydrolysis, this condensation is the best means for preparing the acid in quantity. The imide crystallises from dilute alcohol in stellate clusters of needles melting at 179—180°:

0.1588 gave 0.3531 CO₂ and 0.0717 H₂O. C=60.63; H=5.02.

C₁₁H₁₁O₂N₂ requires C=60.8; H=5.1 per cent.

The *ω-imide* of *αα'-dicarbamylcyclopentane-1:1-diacetic acid*,
C₄H₈C $\begin{array}{l} \text{CH}(\text{CO}\cdot\text{NH}_2)\cdot\text{CO} \\ \text{CH}(\text{CO}\cdot\text{NH}_2)\cdot\text{CO} \end{array}$ NH, is formed from the dicyano-

derivative when it is treated with cold, concentrated sulphuric acid. It crystallises from much alcohol in small, colourless prisms, which darken at 285° and carbonise without melting at 310°:

0.1166 gave 0.2219 CO₂ and 0.0631 H₂O. C=51.88; H=6.01.

0.1620 „ 23.4 c.c. N₂ at 15.5° and 751.5. N=16.62.

C₁₁H₁₅O₄N₃ requires C=52.2; H=5.9; N=16.6 per cent.

Complete hydrolysis of the above compounds with 60 per cent. sulphuric acid leads to *cyclopentane-1:1-diacetic acid*.

Methyl isoPropyl Ketone (XXVI, p. 692).

This ketone does not condense with cyanoacetamide. The condensation with ethyl cyanoacetate has already been carried out by Guareschi (*Atti R. Accad. Sci. Torino*, 1901, 50, 288), but he did not analyse the product.

We find that 8.6 grams of the ketone when treated with 22.6

grams of ethyl cyanoacetate and 50 c.c. of alcoholic ammonia (12 per cent.) give 3.2 grams of the condensation product, which is the ω -imide of $\alpha\alpha'$ -dicyano- β -methyl- β -isopropylglutaric acid (XXVII, p. 692). It crystallises from alcohol in lustrous plates which melt at 233—234°:

0.1271 gave 0.2815 CO_2 and 0.0656 H_2O . C=60.40; H=5.74.

0.1603 „ 26.1 c.c. N_2 at 9° and 756 mm. N=19.40.

$\text{C}_{11}\text{H}_{13}\text{O}_2\text{N}_3$ requires C=60.3; H=5.9; N=19.2 per cent.

β -Methyl- β -isopropylglutaric acid (XXVIII, p. 692) is produced when the above imide is hydrolysed with 60 per cent. sulphuric acid. It crystallises from benzene in small plates melting at 100°:

0.1315 gave 0.2761 CO_2 and 0.0994 H_2O . C=57.26; H=8.40.

$\text{C}_9\text{H}_{10}\text{O}_4$ requires C=57.4; H=8.5 per cent.

β -Methyl- β -isopropylglutaric anhydride, $\text{Pr}^a \text{Me} \text{C} \begin{matrix} \text{CH}_2 \cdot \text{CO} \\ \text{CH}_2 \cdot \text{CO} \end{matrix} \text{O}$,

is prepared by boiling the acid for a short time with acetyl chloride. It crystallises from light petroleum (b. p. 60—80°) mixed with a small quantity of the same solvent boiling at 80—100° in glistening plates melting at 41—42°:

0.1181 gave 0.2740 CO_2 and 0.0880 H_2O . C=63.28; H=8.28.

$\text{C}_9\text{H}_{14}\text{O}_5$ requires C=63.5; H=8.2 per cent.

Methyl ψ -Butyl Ketone (XXIX, p. 692).

This ketone was prepared by the hydrolysis of ethyl methyl-ethylacetoacetate according to the directions of Wislicenus (*Annalen*, 1883, **219**, 303). It does not condense with cyanoacetamide, but gives with ethyl cyanoacetate a very small yield of the ω -imide of $\alpha\alpha'$ -dicyano- β -methyl- β - ψ -butylglutaric acid (XXX, p. 692), a substance which crystallises from alcohol in magnificent, nacreous plates resembling naphthalene in appearance, and melting at 215—216°:

0.0827 gave 0.1860 CO_2 and 0.0471 H_2O . C=61.33; H=6.33.

0.0553 „ 8.65 c.c. N_2 at 16.5° and 770 mm. N=18.36.

$\text{C}_{12}\text{H}_{15}\text{O}_2\text{N}_3$ requires C=61.8; H=6.44; N=18.0 per cent.

Benzylethylmethyl Ketone (XXXI p. 692).

The ketone required for this investigation was prepared according to Harries and Müller's method (*Ber.*, 1902, **35**, 966). The yield of condensation product with ethyl cyanoacetate and

alcoholic ammonia was found to be exceedingly small—0.5 gram being obtained from 8.1 grams of the ketone. The ω -imide of α,α' -dicyano- β -methyl- β -(α -benzylethyl)glutaric acid (XXXII, p. 692) crystallises from dilute alcohol in small needles melting at 223–224°:

0.1212 gave 0.3068 CO₂ and 0.0636 H₂O. C=69.05; H=5.83.
C₁₇H₁₇O₂N₃ requires C=69.2; H=5.8 per cent.

Benzyl isoPropyl Ketone (XXXIII, p. 692).

The pure ketone was prepared by distilling together an intimate mixture of calcium phenylacetate and calcium isobutyrate in a current of carbon dioxide. The product was fractionated and separated into three main fractions, consisting of diisopropyl ketone, benzyl isopropyl ketone, and dibenzyl ketone. After refractionation, 30 grams of benzyl isopropyl ketone were obtained from 165 grams of calcium phenylacetate. The ketone boils at 238–240°. The semicarbazone is formed when a solution of semicarbazide acetate is mixed with the ketone, together with enough alcohol to bring the latter into solution, and the mixture allowed to remain overnight. It crystallises from alcohol in small, cubical crystals resembling common salt, and melts at 138° to a colourless, opaque liquid, which clears at 139°:

0.1454 gave 25.8 c.c. N₂ at 28° and 762.4 mm. N=19.38.
C₁₂H₁₇ON₃ requires N=19.2 per cent.

No condensation product could be obtained from this ketone either with cyanoacetamide or with ethyl cyanoacetate.

When a commercial preparation of the ketone was employed, a condensation product was obtained in poor yield; from this, two compounds were isolated by fractional crystallisation from alcohol. One of these crystallised in clusters of prismatic needles melting at 214–216°, and was proved by direct comparison to be identical with the benzylethyl compound (*q.v.*) (Found: C=68.21; H=5.36; N=15.17. C₁₆H₁₅O₂N₃ requires C=68.3; H=5.3; N=14.9 per cent.).

The other compound can be obtained from the mother liquors after the above compound has separated out, although, with one sample of the ketone, it formed the greater part of the condensation product. It crystallised from alcohol in long, flattened needles melting at 246–247°, and was proved by direct comparison to be identical with the benzylmethyl compound (*q.v.*) (Found: C=67.53; H=5.09. C₁₅H₁₃O₂N₃ requires C=67.4; H=4.9 per

cent.). This compound appears to be identical with the one described by Guareschi as the benzylisopropyl derivative (*Gazzetta*, 1918, **48**, 97).

Benzyl Ethyl Ketone (XXXVII, p. 692).

A condensation product with ethyl cyanoacetate was readily obtained from this ketone, and was prepared for the sake of comparing it with that obtained from benzyl isopropyl ketone. We find the yield to be as high as 7.5 grams from 14.8 grams of the ketone (compare Guareschi, *Gazzetta*, 1918, **48**, 92).

The *ω*-imide of *αα'*-dicyano-*β*-benzyl-*β*-ethylglutaric acid (XXXVI, p. 692) crystallises from alcohol in fine, prismatic needles melting at 214–216° (Guareschi, *loc. cit.*, gives 222–226° as the melting point of this substance):

0.1192 gave 0.2984 CO₂ and 0.0566 H₂O. C=68.27; H=5.28.

C₁₆H₁₅O₂N₃ requires C=68.3; H=5.3 per cent.

The products obtained by the acid hydrolysis of this imide appear to be abnormal, and are still under investigation.

Benzyl Methyl Ketone (XXXV, p. 692).

This ketone condenses very readily with ethyl cyanoacetate and gives a good yield (13 grams from 10 grams of the ketone) of the *ω*-imide of *αα'*-dicyano-*β*-benzyl-*β*-methylglutaric acid (XXXIV, p. 692). It crystallises from alcohol in long, flattened needles, which melt at 246–247° and decompose a few degrees above this temperature:

0.1194 gave 0.2938 CO₂ and 0.0506 H₂O. C=67.12; H=4.71.

0.1076 „ 0.2650 CO₂ (by CrO₃ method). C=67.40.

C₁₅H₁₃O₂N₃ requires C=67.4; H=4.9 per cent.

THE IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,

SOUTH KENSINGTON.

[Received, June 3rd, 1919.]

LVIII.—"*Blue John*" and other Forms of Fluorite.

By BERTRAM BLOUNT and JAMES HARRY SEQUEIRA.

A GOOD deal of work has been done on the properties of fluorspar or fluorite in the various forms in which it occurs in nature. Fluorspar as an industrial substance is ably dealt with in a memoir of the Geological Survey, entitled "Special Reports on the Mineral Resources of Great Britain," by Messrs. Carruthers, Pocock, and May, to which Messrs. Dewey and Brownhead have contributed. In this pamphlet, no reference is made to the cause of the colour.

Derbyshire is properly regarded as the home of "Blue John." The famous Blue John mine is in the Castleton district, and is thus described. "The Blue John mine consists of a number of natural caverns in carboniferous limestone connected by tortuous pipes or fissures and extending for a great distance. The blue fluorspar or 'Blue John' occurs as a lining on the walls of fissures and pipes, or in concentrically arranged layers. It is associated with barytes, and a leader of this mineral is usually considered a good guide to a deposit of 'Blue John.' The so-called veins are irregular, flattened pipes running for a while almost horizontally, and then bending sharply up and down and cutting across the bedding. Where a vein is nearly flat, its upper and lower surfaces are lined by coatings of blue fluorspar. . . ." This is enough for the present purpose, and it may be accepted that this is the best account extant of the occurrence of "Blue John" in Great Britain.

There is not much that we have been able to discover in foreign literature except a paper by H. W. Morse (*Proc. Amer. Acad. Arts and Sci.*, 1906), which deals chiefly with the fluorescence of fluorite as studied in the spectroscope, but incidentally touches on some points of interest here. The essential statements are that the cause of the colour may be due to organic matter, and the conclusion arrived at is that "the question as to the cause of the colour of fluorspar still remains in this unsettled state." It is further said that the cause of the odour on heating is doubtful, and, further, that the gases expelled by this means are chiefly carbon dioxide, carbon monoxide, and hydrogen. Tests were made for helium on 10 kilos. of fluorite with a negative result, and the author of the paper feels so doubtful of his conclusion that towards the end of his paper he says: "I saw no reason to question the statement that the colour of fluorite is due to organic matter."

The evidence for and against this view is given in the ensuing notes of experiments made by ourselves.

Chemical Composition of Blue John.

Below are analysis of "Blue John" and of the white parts of the same mineral.

| "Blue John." | Per cent. | White portions of same sample. |
|--------------------------------|-----------|-----------------------------------|
| | | Per cent. |
| Calcium fluoride | 99.69 | 99.71 |
| Alumina and ferric oxide | 0.048 | 0.026 |
| Manganese | nil | nil |
| Magnesia | 0.006 | 0.005 |
| Chlorine | nil | nil |
| Sulphur trioxide | nil | nil |
| Sulphur | trace | trace |
| Phosphorus | 0.09 | 0.08 |

It will be seen that the difference between them is so small as to be almost inappreciable. It will also be noticed that metals such as manganese, which have been regarded as likely to be the cause of the colour, are practically absent.

The natural conclusion is that the colour of "Blue John" is due to some organic dye of animal origin, and that this has been absorbed by certain parts of the "Blue John" as distinct from others. Some support is given to this idea by the fact that there is usually a mechanical line of demarcation between the white and blue portions of typical pieces of "Blue John." This assumption of the cause of colour was tested by systematic extraction of "Blue John," powdered so as to pass a 60 \times 60 mesh sieve, with chloroform, toluene, and aniline. Chloroform extracted 0.11 per cent. of oily matter, toluene 0.04 per cent. of a similar substance, and aniline nothing further. Acetone, nitrobenzene, and naphthalene were also tried, with negative results; the extracted mineral remained as deep a blue as before extraction. A combustion of the extracted material gave C=0.046 per cent., showing that the amount of organic matter must be minute. The hydrogen was 0.17 per cent., but this is probably due to a small quantity of water combined or occluded, and the same remark may apply to the carbon, which may have existed as liquid carbon dioxide in the crystals. The "Blue John" after combustion was colourless.

It may be remarked that all these experiments were made on the mineral direct from the mine. Earlier experiments were made on "Blue John" prepared as ornaments, and at that time the authors were not aware that the handsomest specimens are filled with resinous matter in order to make them easier to handle and

to turn. Probably on this account other chemists have been misled into the belief that the colouring material is organic, because they have found organic matter in the samples which they examined, and supposed that it was of natural origin. It remains a fact, however, that organic matter exists in "Blue John." This organic matter is not affected by a temperature of 150° . When a temperature of about 350° is reached, the "Blue John" decrepitates and the colour disappears.

Gases from "Blue John."

On account of experiments, which will be described later, it was supposed that the colour of "Blue John" might be due to the action of radium, and many trials were made in this direction. As is well known, glass is easily coloured by the rays from radium, and a series of experiments was made by one of us.

While these experiments were proceeding, another method was adopted for the same end. A fairly large quantity (about 50 grams) of "Blue John" direct from the mine, not impregnated by any extraneous resinous material, was heated in a hard glass tube, and the gases were pumped out. After the carbon dioxide, hydrogen, and nitrogen had been removed, the remaining inert gases were examined spectroscopically in a Plücker tube. Argon was present, but helium was not. The deduction is that the gases consisted only of those that occur naturally in rocks and minerals which readily decrepitate.

Green Fluorspar "Green John."

This is similar to "Blue John," but decrepitates with greater violence. Both varieties fluoresce on heating, the light from the green kind being more vivid. Green fluorspar, called conveniently "Green John," and so referred to hereafter, appears to be much rarer than "Blue John," and it was only by the kindness of a friend that a specimen of good quality was obtained. Others taken from mines in Durham and Cornwall were evidently less pure. As the quantity of good "Green John" available was somewhat small, our examination of it was necessarily limited, and the gases which are given off on decrepitation were not analysed, the quantity at our disposal being too small for any satisfactory examination.

Systematic experiments by one of us (J. H. S.) were carried out at the London Hospital on the action of radium and X-rays

on various samples of fluorspar. The notes made at the time are here recorded.

(A) "*Blue John*": *Experiments with Radium.*

(1) Two pieces of banded fluorspar ("*Blue John*") were exposed to radium, contact being made with a plate 2.5 cm. square containing 30 milligrams of radium salt under a varnish.

As a result of this exposure, both pieces of spar changed colour, the white parts becoming bright blue and the blue becoming darker. In ten days these changes were well marked.

(2) Pieces of "*Blue John*," "*Green John*," and white fluorspar were similarly exposed. In three days, a bright blue change was noticed in the white fluorspar, the "*Green John*" was slightly darker, and the "*Blue John*" much darker.

(3) Portions of "*Blue John*" were heated in glass tubes, and thereby decolorised. These decolorised specimens were then exposed to radium and to X-rays. The specimen exposed to radium for fourteen days became a light blue. The specimen exposed to X-rays for about twenty-four hours continuously became dark purple.

(4) A small portion of "*Blue John*," banded, was exposed for six hours to X-rays, and turned almost a dark violet colour.

The "*Green John*" exposed for fourteen days was distinctly darker in colour.

(B) *Experiments with X-Rays.*

(1) Half an hour's exposure at 7.5 cm. produced on:

"*Blue John*," slight deepening.

"*Green John*," no change.

Fluorspar, change to violet shade.

The fluorspar, on being replaced in a drawer, returned to almost normal colour.

(2) Half an hour's exposure at 7.5 cm. produced on:

"*Blue John*," slight deepening.

"*Green John*," no change.

Fluorspar, change to violet shade.

The fluorspar returned to almost normal colour.

(3) Forty-five minutes' exposure at 7.5 cm. produced on:

"*Blue John*," more marked change.

"*Green John*," no change.

Fluorspar, more marked change.

The fluorspar almost recovered.

- (4) Ten minutes' exposure at 7.5 cm. produced on:

Fluorspar, light violet colour.

No other change perceptible.

- (5) Half an hour's exposure at 7.5 cm. produced on:

"Green John," fluorescence.

Fluorspar, change as before.

The "Green John," after being carried into a dark room, still fluoresced for about three or four minutes.

Fluorspar in a glass tube also fluoresced, but very slightly.

- (6) Ten minutes' exposure at 7.5 cm. produced on:

"Green John," slight fluorescence (both).

Material after resting for fourteen days:

Fluorspar was pink with one mauve spot.

"Blue John" was darker than when experiments started.

"Green John" did not appear to have changed at all.

The fluorspar in glass was darker than at first.

None of the specimens exposed to X-rays made any change in photographic plates, even after prolonged exposure.

Even after colour changes had been produced by exposures to X-rays and radium, there was no evidence of radioactivity, as shown by exposure of a photographic plate.

From these experiments, it appears that there is no substantial difference between white fluorspar and "Blue John," except in respect of the small amount of organic matter which gives the colour of "Blue John."

The same seems to hold for "Green John" and for the amethystine varieties. It appears that the colouring matter is, after all, organic. The influence of X-rays and of radium on natural fluorspar appears similar to that on glass. The *causa causans* is unknown.

From a series of experiments which have now lasted more than two years, there is no reason to suppose that what in the earlier trials seemed to be a reasonable hypothesis, namely, that the colour of "Blue John" and other varieties of coloured fluorspar owes its origin to radioactive effect, has no foundation.

76, YORK STREET,
WESTMINSTER, S.W. 1.

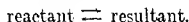
[Received, April 7th, 1919.]

LIX.—*Studies in Catalysis. Part XI. The Le Chatelier-Braun Principle from the Point of View of the Radiation Hypothesis.*

By WILLIAM CUDMORE McCULLAGH LEWIS.

THE object of this note is to point out that the quantum-radiation view of chemical reactivity is in agreement with the thermodynamic principle of Le Chatelier and Braun as applied to the effect of temperature on the equilibrium constant of a reversible reaction.

Consider the reversible reaction:



Let us suppose that the reaction from left to right is endothermic. Then, in accordance with the principle of mobile equilibrium, an increase in temperature will favour the resultants.

From the point of view of radiation, the fact that the above process is endothermic means that the critical increment of the resultant is less than that of the reactant. This follows from the quantum-heat expression:

heat evolved = critical increment of resultant *minus*

critical increment of reactant,

or heat evolved = $Nh(\nu_2 - \nu_1)$, where N is the Avogadro number and h is Planck's constant. In the case considered, it follows that the critical frequency ν_2 of the resultant is less than the critical frequency ν_1 of the reactant.

Let us consider the above equilibrium at two different temperatures, T_1 and T_2 , where T_1 is less than T_2 . For the short infra-red region (which has already been shown to be of significance for reactions which proceed with measurable velocity at the ordinary temperature), as well as for the visible and ultra-violet regions, the radiation density corresponding with the frequency ν_1 at T_1 is

$$\frac{8\pi h\nu_1^3 n^3}{c^3} e^{-h\nu_1/kT_1}$$

and at T_2 the density is

$$\frac{8\pi h\nu_1^3 n^3}{c^3} e^{-h\nu_1/kT_2}$$

where c is the velocity of light in a vacuum.

If T_1 and T_2 are not very far apart, and especially if the react-

ing system is gaseous, the refractive index term n will be practically the same at both temperatures.

The fractional increase in the radiation density, due to the rise in the temperature from T_1 to T_2 at the frequency ν_1 , is given by

$$\frac{\frac{8\pi h \nu_1^3 n^3}{c^3} (e^{-h\nu_1/kT_2} - e^{-h\nu_1/hT_1})}{\frac{8\pi h \nu_1^3 n^3}{c^3} e^{-h\nu_1/kT_1}}$$

which is equal to

$$\left(e^{\frac{h\nu_1}{k} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)} - 1 \right).$$

Similarly, for the fractional increase in the radiation density at the frequency ν_2 we obtain

$$\left(e^{\frac{h\nu_2}{k} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)} - 1 \right).$$

Since by hypothesis ν_1 is greater than ν_2 , it follows from the above expressions that the fractional increase in the radiation density at the frequency ν_1 is greater than that at the frequency ν_2 . Hence at the higher temperature the radiation density of the type absorbable by the reactant (ν_1) has increased *relatively* to that absorbable by the resultant (ν_2).

On the radiation hypothesis of chemical reactivity, it is assumed that the rate of decomposition is directly proportional to the radiation density. For both frequencies, the rise in temperature has caused an increase in the radiation density, but the increase is relatively greater for the higher frequency (ν_1) as compared with the lower frequency (ν_2). It follows, therefore, that at the higher temperature both the reactant and the resultant react or decompose more rapidly than they do at the lower temperature. This is in agreement with experiment. What is more important, however, is that the reactant decomposes at a relatively faster rate than the resultant, because the radiation density of the reactant is relatively increased with respect to that of the resultant. Hence as the temperature is raised, the existence of the resultant, in the above case, is favoured more than that of the reactant, and the equilibrium position shifts over towards the right. Had the reaction been exothermic, the relative positions of ν_1 and ν_2 would have been reversed, with the result that the equilibrium concentration of the reactant would have increased relatively to that of the resultant.

These conclusions are identical with those which are arrived at

on the basis of the principle of Le Chatelier and Braun. The radiation hypothesis is therefore in complete agreement with the thermodynamic generalisation; and, in fact, the conclusion regarding the direction of the change in the equilibrium position with temperature could be inferred on the radiation basis alone, without any direct appeal to thermodynamics.

MUSPRATT LABORATORY OF PHYSICAL AND ELECTRO-CHEMISTRY,
UNIVERSITY OF LIVERPOOL.

[Received, May 29th, 1919.]

Organic Chemistry.

Organic Symbols. INGO W. D. HACKH (*Science*, 1918, 48, 333—335).—The author has evolved a "chemical shorthand" to represent the constitutional formulae of organic compounds, for which is claimed the merits of compactness, exactness, accuracy, clearness, and simplicity. The atoms of the four elements carbon, hydrogen, oxygen, and nitrogen are to be imagined as points in the symbol, and these points are determined by lines (the bonds or valencies of the elements) terminating (hydrogen), meeting (oxygen and nitrogen), or crossing (carbon). Thus, a hydrogen atom is assumed to exist wherever a line ends, an oxygen atom wherever a line makes an angle or two lines meet, a nitrogen atom wherever three lines meet or arise, and a carbon atom wherever two lines cross or four lines radiate. Single bonds are represented by straight lines and double bonds by curved lines. The symbol for acetic acid is therefore $\text{—}\text{C}(=\text{O})\text{—}\text{OH}$. Numerous examples of symbols are given, including those for such complicated substances as morphine, hemoxyprophyrin, and an octadecapeptide. An asymmetric carbon atom is indicated by a dot in the symbol. C. S.

The Atom of Bohr in Organic Chemistry. E. H. BUCHNER (*Chem. Weekblad*, 1919, 16, 521—527).—A theoretical paper in which the author applies the ideas of Rutherford and Bohr regarding atomic and molecular structure to organic compounds. As a consequence of the assumed mode of atomic linking, the symmetrical tetrahedral structure of the methane molecule is deduced, the replacement of one or more hydrogen atoms by substituents causing deformation of the regular tetrahedron. The theory is further applied to the elucidation of the nature of the double bond between carbon atoms. This is shown to differ from the single bond only in the greater radius of the electron orbit, in which four electrons are present instead of two, and in the consequent increased distance between the carbon nuclei. The geometrical isomerism of maleic and fumaric acids, and the transformation of *cis*- into *trans*-forms, are discussed. Kekulé's representation of the benzene molecule as a uniplanar hexagon of alternate singly and doubly linked carbon atoms receives support from the theory. The possible existence of two isomeric ortho-disubstitution products of benzene is admitted, but, owing to the essential qualitative similarity of the single and the double bond, already referred to, it is pointed out that the difference in properties of two such isomerides would probably be imperceptible. W. S. M.

A New Reaction of Paraffin Hydrocarbons. E. V. LYNN (*J. Amer. Chem. Soc.*, 1919, 41, 368—370).—When the reddish-brown solution of nitrosyl chloride in *n*-heptane is exposed to sunlight, CXXVI. i. m

light, it gradually becomes blue and deposits ammonium chloride. The blue colour soon fades, and the turbid liquid then deposits a yellow oil, considerable volumes of hydrogen chloride being evolved. The oil decomposes further when submitted to steam distillation, hydroxylamine remaining in the residue. The distillate is very fragrant, and apparently consists of a mixture of the three *n*-heptanones, although no fraction yielded the *semicarbazone* of dipropyl ketone, m. p. 125°, which was made from calcium butyrate for comparison. Light petroleum exhibits the same phenomena.

In the case of heptane, it is assumed that the main reactions may be represented thus: $C_7H_{16} + NOCl = HCl + C_7H_{15}\cdot NO$ (blue), $C_7H_{15}\cdot ON \rightarrow C_7H_{14}\cdot N\cdot OH$ (oil), and this $+ H_2O = C_7H_{14}O + NH_3\cdot OH$.
J. C. W.

Ethylene. WILLIAM MALISOFF and GUSTAV EGLOFF (*J. Physical Chem.*, 1919, **23**, 65—138).—A résumé of the present state of knowledge of the physical and chemical properties of ethylene, and of the processes of its formation and decomposition. A very full bibliography is given.
W. G.

The Action of Monosodioacetylene on some Halogen Esters of Secondary and Tertiary Alcohols. PICON (*Compt. rend.*, 1919, **168**, 825—828).—The primary alkyl haloids react with monosodioacetylene in liquid ammonia to give homologues of acetylene (compare A., 1913, i, 438; 1914, i, 647). The secondary and tertiary alkyl haloids under similar conditions do not, however, give acetylenic hydrocarbons, but ethylenic hydrocarbons, a molecule of the hydrogen haloid being eliminated; thus:



W. G.

Action of Monosodioacetylene on some Iodides of Primary Alcohols with Branched Chains. PICON (*Compt. rend.*, 1919, **168**, 894—896. Compare preceding abstract).—*iso*Butyl iodide when acted on by monosodioacetylene in liquid ammonia in an autoclave at the ordinary temperature is decomposed, giving *isobutylene*. Commercial *iso*amyl iodide, which is a mixture of the inactive and active forms, under similar conditions yields *isoheptinene* and β -methyl- Δ^2 -butene, together with a condensation product. The *isoheptinene* and the condensation product come entirely from the *i-iso*amyl iodide, whilst the *iso*amylene comes from the active isomeride.

Alkyl iodides of the type $R\cdot CH_2\cdot CH_2I$ yield true acetylenic hydrocarbons when decomposed by monosodioacetylene, whereas from iodides of the types $R\cdot CHR'\cdot CH_2I$ or $R\cdot CH_2\cdot CHR'I$ an ethylenic hydrocarbon is always formed. This formation of an ethylenic hydrocarbon is shown not to be due to the presence of traces of water or to any action of the liquid ammonia on the alkyl iodide.
W. G.

Action of Magnesium Phenyl Bromide on Polyhalogenated

Derivatives of Ethane. FRED. SWARTS (*Bull. Soc. chim.*, 1919, [iv], 25, 145—174).—In an endeavour to prepare difluorobromoethylbenzene by the action of magnesium phenyl bromide on $\alpha\alpha$ -difluoro- $\alpha\beta$ -dibromoethane, the author could only obtain difluoroethylene. He then studied this reaction with a number of other polyhalogenated derivatives of ethane, using, in every case, one molecule of the organomagnesium compound and one molecule of the substituted ethane. The reaction was, in every case, complex and gave rise to several different compounds. In the case of the bromo-derivatives of ethane, the principal reaction consisted in the elimination of two halogen atoms and the formation of an ethylene derivative and bromobenzene. When the halogenated ethane had an atom of fluorine and an atom of bromine attached to the same carbon atom, it was always the atom of bromine which was eliminated. In the case of a compound of the type $\text{CH}_2\text{I}\cdot\text{CHF}_2$, where an atom of fluorine and an atom of iodine were eliminated, the principal reaction always proceeded according to the equation $\text{CH}_2\text{I}\cdot\text{CHF}_2 + \text{MgPhBr} = \text{CH}_2\text{:CHF} + \text{PhI} + \text{MgBrF}$. The chloro-derivatives behaved differently from the fluoro-, bromo-, or iodo-derivatives of ethane in that, instead of two halogen atoms being eliminated, a molecule of hydrogen haloid was eliminated. Thus tetrachloroethane yielded trichloroethylene and $\beta\beta$ -difluoro- $\alpha\alpha$ -dichloroethane yielded fluorodichloroethylene.

In several of the reactions where magnesium fluoride was formed, this salt was obtained in the form of a colloidal solution in water, the salt not being immediately precipitated by the addition of acid, and in certain cases the magnesium fluoride remained dissolved in ether.

In addition to the above general reaction, a number of secondary actions occurred, of which the most constant was the formation of diphenyl. The formation of this compound is most marked where the general reaction is slow, and less noticeable when the reaction is violent.

W. G.

Action of Alkaline Reducing Agents on Iodoform. A.

GUTMANN (*Ber.*, 1919, 52, [B], 212—215).—When iodoform is added to a solution of arsenious oxide in about 27% sodium hydroxide, reaction takes place almost quantitatively, according to the equation $\text{CHI}_3 + \text{Na}_3\text{AsO}_3 + \text{NaOH} = \text{CH}_2\text{I}_2 + \text{NaI} + \text{Na}_3\text{AsO}_4$. Iodoform also oxidises sodium antimonite and stannite, and an alcoholic solution liberates sulphur from fresh sodium sulphide. When warmed with a mixture of sodium sulphide and cyanide, it produces a thiocyanate, but it will not oxidise a sulphide. J. C. W.

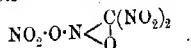
Preparation of Tetranitromethane. KENNEDY JOSEPH

PREVITÉ ORTON (*Brit. Pat.*, 125000).—Acetylene is passed into nitric acid of 90—97.5% strength, preferably at a temperature of about 40°; absorption occurs more readily in the presence of mercury or a mercury salt, whereby also the yield is improved

when the operation is performed at 40°, but not at lower temperatures. The product is now mixed with sulphuric or fuming sulphuric acid under conditions excluding rise in temperature, and the mixture is gradually heated until the tetranitromethane distils, or slowly heated in a reflux apparatus until gas ceases to be evolved and then distilled. Apparently, the chief product of the action of acetylene on nitric acid is an intermediate compound, which is converted into tetranitromethane when the solution is heated with sulphuric acid. [See also *J. Soc. Chem. Ind.*, 1919, June.]
H. W.

Constitution of Tetranitromethane. ERICH SCHMIDT (*Ber.*, 1919, 52, [B], 400—413).—From the results of a quantitative study of the behaviour of tetranitromethane towards aqueous potassium hydroxide, it appears that the substance is decomposed in two ways, according to the equations: (1) $C(NO_2)_4 + 2KOH = KNO_3 + KC(NO_2)_3 + H_2O$ (compare Hantzsch and Rinkenberger, A., 1899, i, 404), and (2) $C(NO_2)_4 + 6KOH = 4KNO_2 + K_2CO_3 + 3H_2O$. The course of the reaction depends on the concentration of the alkali; the ratio of the quantity reacting according to the first equation to that according to the second varies from 2:1 with 0.1*N*-alkali to 12:1 with 14*N*-alkali.

Iodotritnitromethane only reacts in one direction, however, analogous to (1) above: $3CI(NO_2)_3 + 6KOH = 3KC(NO_2)_3 + 2KI + KIO_3 + 3H_2O$ (Hantzsch, A., 1906, i, 617). The dual nature of tetranitromethane is therefore connected with the fourth "nitro"-group, and the facts can be explained on the assumption that the compound exists in the tautomeric forms



(Willstätter and Hottenroth, A., 1904, i, 472) and $NO \cdot O \cdot C(NO_2)_3$. The first form reacts according to equation (1), and is favoured by concentrated alkalis, whilst the second isomeride reacts according to equation (2).

In the quantitative study of the reaction, the following estimations were made: (1) The alkali required in the case of the 0.1*N*-solution. Sealed bulbs of the nitro-compound were crushed under the potassium hydroxide, and the excess of alkali was titrated, using phenolphthalein. (2) The nitrite. Immediately after the reaction with the alkali was completed, the clear solution was neutralised in the cold, and the nitrite estimated as nitrogen by means of ammonium chloride. (3) The carbonate. Some reactions were performed with 0.1*N*-barium hydroxide, and the barium carbonate produced was converted into the sulphate and weighed. (4) The nitrate. The product of the reaction with 0.1*N*-alkali was mixed with palladinised barium sulphate and concentrated potassium hydroxide, and treated with hydrogen until the solution became pale yellow. The nitroform was thereby reduced to an unknown compound, but the nitrate left almost untouched. The

filtered solution was then evaporated, dropped on hydrazine sulphate to decompose the nitrite, diluted, filtered again, acidified with sulphuric acid, and precipitated with nitron acetate. (The preparation of palladiised barium sulphate is described.) (5) The nitroform. The nitrite was decomposed by boiling with ammonium chloride, and then the solution was transferred to a flask with a ground-in still-head, acidified with phosphoric acid, and boiled until the nitroform had passed over, this being trapped in 0.1N-potassium hydroxide. The solution was acidified with acetic acid and precipitated with nitron acetate.

Tetranitromethane also decomposes into a nitrite when treated with dilute hydrochloric acid, for dimethyl-*m*-toluidine can be converted into its *p*-nitroso-compound by such a mixture.

The following salts of nitroform have been prepared: the stable nitron salt, $C_{20}H_{16}N_4, CH(NO_2)_3$, decomp. $136-141^\circ$; *di*-isobutylamine salt, decomp. $121-123^\circ$; *piperidine* salt, notched leaflets, decomp. 100° ; *dibenzylamine* salt, needles, decomp. $160-163^\circ$.

J. C. W.

Preparation of Optically Active Propylene Glycol. AD.

GRÜN (*Ber.*, 1919, 52, [B], 260-263).—Abderhalden has recently isolated the active forms of propylene glycol (this vol., i, 2), but Grün had already studied the subject with the partial success now described.

Propylene glycol is left with concentrated sulphuric acid at the ordinary temperature, and the inactive *dihydrogen disulphate*, $C_3H_7(O\cdot SO_3H)_2$, is isolated as the *barium* salt, $3H_2O$, which is converted into the *potassium* salt. leaflets, 0.5EtOH, *sodium* salt, needles, and *strychnine* salt. Two modifications of the last salt are obtained: pearly tablets, $[\alpha]_D^{20} - 20.38^\circ$, of which 0.9 gram dissolves in 100 c.c. of water, and rosettes of long, slender needles, $[\alpha]_D^{20} - 28.19^\circ$, with the solubility 11.82. By treatment with 0.2N-barium hydroxide, the tablets have been converted into the *barium* salt of *d*-propylene *dihydrogen disulphate*, $[\alpha]_D^{20} + 11.50^\circ$, but further progress in the isolation of *d*-propylene glycol could not be made, owing to the great stability of the free acid ester.

J. C. W.

Some Derivatives of Trimethylene Glycol. ERICH SCHMIDT

and RUDOLF WILKENDORF (*Ber.*, 1919, 52, [B], 389-399).—Henry found in 1895 that "nitroisobutylglycerol," $NO_2\cdot C(CH_2OH)_3$, could be obtained readily by the condensation of nitromethane with formaldehyde under the influence of alkali hydroxides, but all his attempts at controlling the reaction so as to give nitrotrimethylene glycol were unsuccessful. The present authors have also found that partial condensation is hopeless, but have succeeded in making the glycol by the action of sodium methoxide solution on the glycerol, one molecule of formaldehyde being eliminated.

Nitroisobutylglycerol [nitrotrihydroxymethylmethane] is produced in 79% yield by warming a solution of nitromethane and

paraformaldehyde in dry ethyl acetate with a few drops of 33% potassium hydroxide. This is an improvement on Henry's method (A., 1896, i, 4). The *tribenzoate*, $\text{NO}_2\cdot\text{C}(\text{CH}_2\cdot\text{OBz})_3$, obtained by the action of benzoyl chloride and quinoline, crystallises in needles, m. p. 111° . The trihydric alcohol may also be prepared in methyl-alcoholic solution, and if such a solution is chilled and slowly mixed with sodium methoxide solution, *sodiumnitrotrimethylene glycol*, $\text{NO}_2\cdot\text{CNa}(\text{CH}_2\cdot\text{OH})_3$, separates in small prisms with 2MeOH , which crystallise with $2\text{H}_2\text{O}$ from aqueous alcohol, the yield being 91%. The salt decomposes vigorously at $130\text{--}136^\circ$, and gives the red colour with ferric chloride and the blue with ethereal hydrogen chloride, characteristic of the salts of nitro-paraffins. The salt is converted into free *nitrotrimethylene glycol* by boiling with ethereal salicylic acid. The compound crystallises from a mixture of ethyl acetate and chloroform in groups of feathery needles, m. p. $56\text{--}58^\circ$, is soluble in oxygenated solvents, does not give a colour with ferric chloride, is neutral to litmus, reduces ammoniacal silver oxide, decomposes when treated with benzoyl chloride and quinoline, and condenses with formaldehyde to give the above *nitroisobutylglycerol*.

If the sodium salt is treated with ethereal bromine, it gives a 97% yield of *bromonitrotrimethylene glycol*, which crystallises in groups of stout prisms, m. p. $120\text{--}122^\circ$, and forms a *dibenzoate*, $\text{NO}_2\cdot\text{CBr}(\text{CH}_2\cdot\text{OBz})_3$, in highly refractive prisms, m. p. 104° .

The nitro-compound is reduced by means of hydrogen, catalysed by palladinised barium sulphate, in oxalic acid solution. *Amino-trimethylene glycol* is a strongly alkaline syrup with a bitter taste, and forms a snow-white *oxalate*, decomp. 202° . When benzoylated by the Schotten-Baumann method, it yields the *N-benzoyl* derivative, which crystallises in delicate needles, m. p. 131° , with a bitter taste, whereas in the presence of quinoline the *tribenzoyl* derivative, $\text{NHPr}_2\cdot\text{CH}(\text{CH}_2\cdot\text{OBz})_3$, is formed. This crystallises in needles, m. p. 136° , which no longer taste bitter. J. C. W.

Dichloroethyl Sulphide (Mustard Gas). III. Solubility and Hydrolysis of Dichloroethyl Sulphide with a New Method for Estimating Small Amounts of the Same.

F. F. HOPKINS (*J. Pharm. Expt. Ther.*, 1919, 12, 393—403).—The solubility of dichloroethyl sulphide in water has been determined, and at 10° has been found to be approximately 0.07%. The velocity of hydrolysis of dichloroethyl sulphide has been measured at 0.6° , 10° , 20° , 30° , and 37.5° ; the data are graphically represented in a series of curves. The hydrolysis is found to follow the equation for a unimolecular reaction.

Dichloroethyl sulphide in admixture with air may be rapidly estimated by bubbling the gas through a series of two tubes containing water at 35° ; the gas is rapidly absorbed and hydrolysed, and the hydrogen-ion concentration of the solution is then measured, methyl-red being used as indicator. It is necessary that all the glassware used should be insoluble in water. H. W.

Mercury Mercaptide Nitrites and their Reaction with the Alkyl Iodides. VI. Chain Compounds of Sulphur (*continued*).
SIR PRAFULLA CHANDRA RÂY (T., 1919, 114, 548—552).

Preparation and Hydrolysis of Esters Derived from the Substituted Aliphatic Alcohols. GEORGE R. BANCROFT (*J. Amer. Chem. Soc.*, 1919, 41, 424—431. Compare A., 1918, i, 2).—A study of the rate of hydrolysis by 0.1*N*-hydrochloric acid of the acetates of β -chloroisopropyl, $\beta\beta'$ -dichloroisopropyl, $\beta\gamma$ -dichloro- and $\beta\gamma$ -dibromo-propyl alcohols. As in the case of β -substituted ethyl acetates, it is found that the presence of a halogen atom in the β -position retards hydrolysis, the influence being still more pronounced in the case of $\beta\gamma$ -disubstituted esters, but most striking in the case of esters with two halogens in the β - and β' -positions.

The esters were obtained as follows: $\beta\beta'$ -dichloroisopropyl acetate, b. p. 201—203°, by the action of acetyl chloride on $\beta\beta'$ -dichlorohydrin; $\beta\gamma$ -dichloropropyl acetate, b. p. 197—198°, in a similar manner, the alcohol being formed by chlorinating allyl alcohol; β -chloroisopropyl acetate, b. p. 149—150°, in the same way, the alcohol being obtained by adding concentrated sulphuric acid to allyl chloride at 0°, and then, after keeping a day, diluting with water and boiling, thus: $\text{CH}_2=\text{CH}\cdot\text{CH}_2\text{Cl} + \text{H}_2\text{SO}_4 \rightarrow \text{CH}_2\text{Cl}\cdot\text{CHMe}\cdot\text{SO}_3\cdot\text{OH} \xrightarrow{\text{H}_2\text{O}} \text{OH}\cdot\text{CHMe}\cdot\text{CH}_2\text{Cl} + \text{H}_2\text{SO}_4$; the alcohol is isolated by distilling the solution (up to 130°), neutralising the distillate with potassium carbonate, saturating with salt, and extracting with ether.

In the preparation of allyl chloride by the action of phosphorus trichloride on allyl alcohol, advantage may be taken of the insolubility of the chloride in water to separate it from the phosphorous acid.
J. C. W.

Preparation of *iso*Butyl Oleate. ERNST PREISWERK (*Brit. Pat.*, 123685).—*iso*Butyl oleate, prepared by condensing oleic acid or its chloride with *isobutyl* alcohol by the usual methods, has b. p. 190°/4 mm. and D_{20}^{20} 0.86. It is insoluble in water and possesses healing properties in cases of tuberculosis.

Hydrolysis of Glycollide and Lactide in Acid Solution. HJALMAR JOHANSSON and HUGO SEBELIUS (*Ber.*, 1919, 52, [B], 745—752).—Glycollide and lactide are hydrolysed by water to glycollic and lactic acids with intermediate formation of glycollo-glycollic and lacto-lactic acids respectively: $\text{O} \begin{smallmatrix} \diagup \text{CO}\cdot\text{CH}_2 \\ \diagdown \text{CH}_2\cdot\text{CO} \end{smallmatrix} \text{O} + \text{H}_2\text{O} = \text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OH}$; $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OH} + \text{H}_2\text{O} = 2\text{OH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$. The authors have particularly investigated the first phase of the reaction, since the second is known to proceed normally. It occurs too rapidly in alkaline solution to permit accurate measurement. In moderately acid solution, the change takes the form of two independent, simultaneous reactions, only one of which is catalysed by hydrogen ions.

It therefore appears that hydrolytic fission of β -lactones is catalysed slightly or not at all by hydrogen ions, that of γ -lactones is catalysed, whilst the opening of the six-membered ring of glycolide or lactide proceeds either with or without catalytic assistance of hydrogen ions.

The experiments were carried out by adding solutions of glycolide or lactide in anhydrous acetone to water or dilute acid at $19.8 \pm 0.1^\circ$; at suitable intervals, aliquot portions of the solution were added to a solution of potassium iodide and potassium iodate, and the liberated iodine was estimated by titration with sodium thiosulphate after allowing sufficient interval for the complete liberation of iodine. The results are probably slightly low, the error, however, not exceeding 1%. The presence of acetone does not affect the titration, whilst the secondary hydrolysis of the ester acid occurs so slowly that it need not be taken into account.

H. W.

The Basic Properties of Oxygen in Organic Acids and Phenols; and the Quadrivalency of Oxygen. JOSEPH KNOX and MARION BROCK RICHARDS (T., 1919, 114, 508—531).

Pasteur's Principle of the Relation between Molecular and Physical Asymmetry. VIII. On the Spontaneous Fission of Racemic Potassium-Cobaltioxalate into its Optically Active Antipodes. F. M. JAEGER and WILLIAM THOMAS (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, 21, 693—706).—When an aqueous solution of inactive potassium cobaltioxalate is allowed to crystallise at temperatures near 0° , the racemic salt separates in the form of dark green, almost black triclinic pinacoidal crystals of the composition $K_3\{Cr(C_2O_4)_3\}3\frac{1}{2}H_2O$, D^{25}_D 1.877. These crystals are not isomorphous with those of the corresponding triclinic chromium, rhodium, and iridium salts, the water content being different (A., 1918, i, 3). When, however, the inactive solution is allowed to crystallise near 18° , separate crystals of the *d*- and *l*-compounds are deposited. These have trigonal trapezohedral symmetry, and are isomorphous with the corresponding optically active rhodium and iridium salts: $\alpha:c=1:0.8968$, α $100^\circ 27'$, D^{25}_D 1.8893. Only on rare occasions could the *d*- and *l*-crystals be distinguished by the presence of hemihedral faces, in spite of their enormous optical activity. This is the first fully substantiated example of the spontaneous fission into its components of such a racemic complex metallic compound. The transition temperature of the racemic compound into its components, determined by the solubility method, was found at 13.2° .

The dark green solution of the active salt shows a pronounced absorption band between 5510 and 6520 Å.U. The form of the rotatory dispersion curve is noteworthy. The molecular rotation increases rapidly with increasing wave-length, but in the vicinity of the absorption band falls steeply, assuming the opposite algebraic sign at about 6260 Å.U., and reaching a maximum in the other

direction at about 6400 Å.U. The curve is similar in type to that of potassium chromium oxalate, the latter, however, showing a much greater absolute rotation on either side of the zero line. The positions of the maxima and minima are also different in the two salts, corresponding with the different positions of the absorption bands. For certain wave-lengths, the two *d*-forms (or *l*-forms) actually have opposite rotations. The influence of the specific nature of the central metallic atom is shown in the fact that the potassium rhodium- and iridium-oxalates have normal rotatory dispersion curves.

E. H. R.

The Supposed Diastatic Properties of Formaldehyde.

HERMANN SALLINGER (*Ber.*, 1919, 52, [B], 651—656).—A further contribution to the controversy on this subject (compare Woker, A., 1917, i, 61, 447; Kaufmann, A., 1917, i, 251). The author considers that the only valid evidence of the enzymatic indifference of formaldehyde towards starch is obtained by observation of the specific rotation and absence of reducing power towards Fehling's solution which can be ascribed to the action of formaldehyde on starch. With regard to the first point, a solution of amylopectrin (Lintner) is found to retain its optical activity unchanged after digestion with formaldehyde during forty-four hours at 37°, thus confirming Kaufmann's previous observation. With regard to the second point, a solution of soluble starch (Wolff, Fernbach), after treatment with formaldehyde and removal of the latter as completely as possible, only showed slight reducing power towards Fehling's solution, which depended on traces of residual formaldehyde. Further, in a comparative series of experiments in which formaldehyde solutions of differing concentration were mixed on the one hand with starch solution and on the other with water, and subsequently treated with Fehling's solution, a greater reduction was not found in any instance in the solutions containing starch than in those from which it was absent. The author therefore considers formaldehyde to be enzymatically indifferent to starch.

H. W.

The Relations between the Chemical Structures of Carbonyl Derivatives and their Reactivities toward Salts of Semicarbazide. ARTHUR MICHAEL (*J. Amer. Chem. Soc.*, 1919, 41, 393—424).—The velocities of the reactions of aldehydes and ketones with various reagents have been investigated quantitatively, chiefly by Petrenko-Kritschenko, and the results discussed in their theoretical aspects (see Stewart, "Stereochemistry," 474—501). The velocity factor in such reactions depends mainly on the magnitude of the free chemical energy of the carbonyl group and on its affinity relationships to the component parts of the reagent. From a determination of the reaction velocities of different ketones towards the same agent, conclusions may be drawn as to the influence of structure on the free energy of the carbonyl group, but this is not necessarily the same as discussing the reactivity of the

m^*

ketone. Reactivity is frequently confused with instability, but the latter term should be restricted to the behaviour of a compound towards physical forces, and the former used only in reference to the behaviour of a certain atom or group of atoms in a given chemical system. The reactivity of a ketone, for example, is the sum total of the changes in the free and bound chemical energy in all the atoms, manifesting itself at the carbonyl group because the hindrance to chemical change is best overcome at this point.

The present investigation has for its chief aim the arrangement of groups of carbonyl derivatives according to the relative reactivities of the members towards certain reagents. For such a purpose, semicarbazide is the most suitable agent, since its salts are only slightly hydrolysed in solution and most semicarbazones are only sparingly soluble in water. As a preliminary to the formation of a semicarbazone from a salt of semicarbazide, a carbonyl derivative must liberate the base, that is, it must exert as much energy as was dissipated in the neutralisation of the base by the acid. Since semicarbazide is a strong base, this energy will stand in direct relation to the affinity constant of the acid. The reactivity of a carbonyl compound can therefore be gauged by finding at what limit it ceases to react with a series of semicarbazide salts. Some carbonyl derivatives react with salts of semicarbazide and the strongest mineral acids. In such cases, the limit is ascertained by adding some of the free acid and finding how much is necessary to prevent reaction, or, in other words, to make the reverse hydrolysis of the semicarbazone to proceed with equal velocity. A similar method is employed in the case of two carbonyl derivatives which both react with the semicarbazide salt of one acid, but not with the salt of the next stronger acid; the more reactive compound is the one which forms a semicarbazone in the presence of the greater amount of the free acid.

Semicarbazide, m. p. 95°, and the following salts were employed in the experiments: hydrochloride, m. p. 175°; hydrogen sulphate, m. p. 145° (decomp.); sulphate, m. p. 143°; formate, m. p. 126°; benzenesulphonate, plates, m. p. 187° (decomp.); acetate, m. p. 75°; chloroacetate, m. p. 111—112°; dichloroacetate, m. p. 108°; trichloroacetate, m. p. 154° (decomp.); oxalate, m. p. 133° (decomp.); maleate, m. p. 100°; hydrofluoride; salicylate, m. p. 153°; *o*-nitrobenzoate, m. p. 96°.

These salts and mixtures of them with the free acids fall into the following order when the difficulty of a ketone to liberate and react with the base is considered: (1) free base; (2) acetate; (3) formate; (4) chloroacetate; (5) oxalate; (6) dichloroacetate; (7) dichloroacetate + 0.5*N*-acid; (8) trichloroacetate; (9) hydrochloride; (10) hydrochloride + 0.2*N*-HCl; (11) hydrochloride + 0.5*N*-HCl; (12) hydrochloride + 0.6*N*-HCl; (13) hydrochloride + 0.6*N*-HCl; (14) hydrochloride + 1.0*N*-HCl. This order, therefore, may be regarded as the scale of reactivity.

In the first series of experiments, the reactions between aliphatic ketones and these agents in aqueous solution are described. For

the purpose, 0.5 mg.-mol. of the ketone was shaken with 0.8 c.c. of a solution containing 0.56 mg.-mol. of the salt, and any precipitates were purified and examined. No experiment was considered negative under 200 hours. The origins of the ketones are summarised, and the results are described in detail, discussed at some length, and reproduced by curves, particular attention being paid to the influence of branched chains. The least reactive ketone is propyl isopropyl ketone (1 on the scale), and the most reactive are methyl hexyl (12) and methyl octyl ketones (15). Dimethyl, diethyl, and dipropyl ketones come about 6 on the scale.

In a second series of experiments, alcoholic media were employed, 0.5 mg.-mol. of the ketone in 0.85 c.c. of alcohol of D 0.9270, or 0.9097 for the highest members, was shaken with 0.5 mg.-mol. of the reagent in the same volume of the same alcohol, and then at different intervals up to five months a few drops of the solution were evaporated and tested for a semicarbazone. Under such conditions, practically all the ketones only react with the free base; only the higher members, such as methyl hexyl ketone (10), show any great reactivity. The insolubility of the semicarbazone is obviously of considerable importance, but even in these cases in which the mixture remains homogeneous there is no connexion between reactivity and reaction velocity. Methyl hexyl ketone, for example, has the largest reactivity with semicarbazide in alcohol, but the velocity of its reaction with phenylhydrazine is only about half, and its velocity with potassium hydrogen sulphite about one-quarter, of the acetone velocities.

Acetophenone takes the ninth place on the scale and propiophenone about the fourth.

With the aldehydes, the outstanding feature is the great reactivity of formaldehyde and the aromatic aldehydes. These all react with semicarbazide hydrochloride even in the presence of 10N-hydrochloric acid. The changes from $\text{H}\cdot\text{CHO}$ to $\text{Me}\cdot\text{CHO}$ and $\text{C}_6\text{H}_5\cdot\text{CHO}$ to $\text{C}_6\text{H}_5\cdot\text{COMe}$ are accompanied by great falls in reactivity.

Several ketonic esters have also been investigated. Ethyl acetoacetate is much more reactive than the alkylacetoacetates, $\text{COMe}\cdot\text{CHR}\cdot\text{CO}_2\text{Et}$ and $\text{COMe}\cdot\text{CR}_2\cdot\text{CO}_2\text{Et}$, and is more reactive than ethyl benzoylacetate.

The following appear to be new: *methyl octyl ketone semicarbazone*, m. p. 119° ; *ethyl methylacetoacetate semicarbazone*, pale blue crystals, m. p. $183\text{--}187^\circ$ (decomp.); *ethyl ethylacetoacetate semicarbazone*, m. p. 154° (decomp.); *ethyl dimethylacetoacetate semicarbazone*, m. p. $183\text{--}187^\circ$ (decomp.); *ethyl allylacetoacetate semicarbazone*, m. p. 125° ; *ethyl diacetylmalonate semicarbazone*, $\text{C}_{13}\text{H}_{21}\text{O}_6\text{N}_3$; *ethyl oraloacetate semicarbazone*, m. p. 169° ; *ethyl benzoylacetate semicarbazone*, m. p. 125° (decomp.).

Some practical applications of the above classification of the ketones may be mentioned. In the first place, a scheme for the separation of a mixture of ketones could be designed, based on the treatment of the mixture with solutions of semicarbazide salts in

decreasing order of the strengths of the acids. Secondly, strong acids may be classified according to their reactivities in concentrated solutions by finding what excess of acid is necessary to inhibit the formation of the semicarbazone of a suitable ketone.

J. C. W.

Mutarotation of Dextrose and Lævulose. J. M. NELSON and FRANK M. BEEGLE (*J. Amer. Chem. Soc.*, 1919, **41**, 559—575).—The specific rotation of α -*D*-glucose, β -*D*-glucose, and β -*D*-fructose has been determined at 0.15°, 15°, 25°, and 37°. The values found are: α -*D*-glucose, +111.2°; β -*D*-glucose, +17.5°; and β -*D*-fructose, -130.8°. These values are constant for all the temperatures investigated. The relation between the rate of mutarotation of the three sugars and varying concentrations of hydrogen ion has been determined. It is shown that the equilibrium rotation of dextrose is not affected by temperature, whilst that of lævulose varies with the temperature of the solution. The mutarotation of dextrose appears to be simply racemisation, whilst that of lævulose is not. The mutarotation of dextrose and lævulose in the presence of each other and in the presence of sucrose and invertase has been measured, and in each case was found to be independent of the other when present, except in the case of solutions of lævulose and sucrose, when the rate of mutarotation and the rotation at equilibrium were affected. The temperature-coefficient of the mutarotation was also determined.

J. F. S.

Glycollonitrile-*D*-glucoside, $C_6H_{11}O_5 \cdot O \cdot CH_2 \cdot CN$. EMIL FISCHER (*Ber.*, 1919, **52**, [B], 197—200. Compare A., 1917, i, 658).—The isolation of *glycollonitrile-*D*-glucoside* by the hydrolysis of its tetra-acetyl derivative with methyl-alcoholic ammonia is now described. It is an amorphous substance, $[\alpha]_D^{20} -45.97^\circ$, which is soluble in cold water or pyridine, but not in most indifferent organic media, and it is very susceptible to hydrolytic influences. It is not so readily affected by emulsin, however, as mandelonitrile glucoside is, the best conditions being when the *H*-ion concentration is about $10^{-5.2}$. Hydrogen cyanide is formed during the hydrolysis. Proof of the purity and identity of the compound lies chiefly in its re-acetylation to tetra-acetylglucosidoglycollonitrile.

J. C. W.

Syntheses of Linamarin and Glycollonitrile Celloside. EMIL FISCHER and GERDA ANGER (*Ber.*, 1919, **52**, [B], 854—868).—The synthesis of linamarin, effected on lines similar to those followed by Fischer and Bergmann (A., 1917, i, 657) in the syntheses of mandelonitrile glucoside and sambunigrin, has already been described (A., 1918, i, 526).

Ethyl tetra-acetylglucosido- α -hydroxyisobutyrate is converted by aqueous barium hydroxide into *glucosido- α -hydroxyisobutyric acid*, prisms, m. p. 146—147° (corr.), $[\alpha]_D^{20} -23.06^\circ$ in water. The physical constants of the synthetic linamarin differ slightly from those recorded for the natural substance, particularly in respect

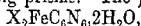
to optical activity, but the differences are not sufficiently great to cause any doubt as to the identity of the products. Both the synthetic and natural glucosides are slowly hydrolysed by emulsin, more rapidly by phaseolunataase from *Phaseolus lunatus*. The substance is in all probability a β -glucoside, since it is the result of a type of synthesis which in all previous instances has led to β -glucosides, and since all the successive products are levorotatory, whilst, in general, the α -glucosides are dextrorotatory.

Since amygdalin, the most important representative of the cyanogenetic glucosides, is a derivative of a disaccharide, the authors have extended the synthesis to similar sugars, and have prepared the compound of cellose with glycollonitrile on lines similar to those used for linamarin.

Ethyl hepta-acetylcellosidoglycollate, needles, m. p. 161—163° (corr.), $[\alpha]_D^{25} - 30.9^\circ$ in acetone, is prepared from acetobromocellose, ethyl glycollate, and dry silver oxide, and is converted by methyl-alcoholic ammonia into *cellosidoglycollamide*, prisms, m. p. 150—152° (corr.), $[\alpha]_D^{25} - 27.9^\circ$ in water, which is hydrolysed by emulsin with the formation of dextrose. The amide is converted in the usual manner into *cellosidoglycollamide hepta-acetate*, slender needles, m. p. 205—206° (corr.), $[\alpha]_D^{25} - 20.6^\circ$ in acetone, which, when treated with phosphorus oxychloride, passes into *cellosidoglycollonitrile hepta-acetate*, small needles, m. p. 200—202° (corr.) after previous softening, $[\alpha]_D^{25} - 26.68^\circ$ in acetone. The latter, on deacetylation, gives *cellosidoglycollonitrile*, $\text{CN}\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_{12}\text{H}_{21}\text{O}_{10}$, which could only be obtained as an amorphous mass, frequently of a pale yellow colour; when heated, it softens at about 80°, and is slowly converted into a viscous mass, which evolves gas at about 108°. It has $[\alpha]_D^{25} - 28.74^\circ$ in water. When reacylated by acetic anhydride in pyridine solution, it gives the original hepta-acetate in good yield. It is hydrolysed by emulsin with comparative ease, giving hydrocyanic acid and dextrose. H. W.

Alkylaminochromi-compounds. III. H.J. MANDAL (*Ber.*, 1919, 52, [B], 330—341. Compare A., 1916, i, 202, 792).—The following *chloropentapropylaminochromic* salts are described: The *chloride*, $[\text{CrCl}(\text{NH}_2\text{Pr})_5]\text{Cl}_2$, is obtained by the action of propylamine on chromic chloride at as low a temperature as possible, a dichlorotetrapropylaminochromic chloride being formed if the reaction is not well controlled. It crystallises in red tablets from water, in which 1 part is soluble in 35 parts at the ordinary temperature, and it gives up propylamine at 60—70°. Other salts are prepared as precipitates from the red solution of the chloride by double decomposition or addition of a suitable chloride. The *bromide* requires nearly twice, and the *iodide* nearly three times, as much water for solution. The *mercurichloride*, $3\text{XCl}_2.4\text{HgCl}_2$, is pale violet; the *mercuribromide*, XHgBr_4 , is very pale reddish-violet; the *mercuri-iodide*, XHgI_4 , is still paler; the *platinichloride*, $\text{XPtCl}_6\cdot\text{H}_2\text{O}$, has the colour of chamois; the *bismuthichloride*, $\text{X}_3\text{Bi}_2\text{Cl}_{12}$, is a pale reddish-violet powder; and

the *stibichloride*, XSbCl_5 , forms very minute, indefinite crystals. The *hydrogen sulphate*, $\text{X}(\text{HSO}_4)_2$, crystallises in glistening, violet scales; the *dithionate*, XS_2O_6 , forms violet, hexagonal tablets; and the *sulphide*, XS_3 , is a yellowish-brown powder. The *nitrate*, $\text{X}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, forms long prisms. The *ferrocyanide*,



is pale red, but becomes yellowish-brown in the light, and is about the most insoluble salt of the series; the *ferricyanide*, $\text{X}_3(\text{FeC}_6\text{N}_6)_2$, is yellow with a tinge of red, and the *chromicyanide*, $\text{X}_3(\text{CrC}_6\text{N}_6)_2$, is a reddish-violet, microcrystalline powder. The *trioxalocobaltiate*, $\text{X}_3[\text{Co}(\text{C}_2\text{O}_4)_3]_2$, is a bluish-green, crystalline powder, and the *trioxalochromiate*, $\text{X}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]_2$, crystallises in brownish-violet, glistening bundles of minute needles. The dichromate is soluble, but the *chromate*, XCrO_4 , is a very sparingly soluble, yellow powder.

J. C. W.

Xanthates of Quaternary Ammonium, Sulphine, and Analogous Bases. JAIME FERRER (*Anal. Fis. Quim.*, 1918, 16, 724—727).—Quaternary ammonium bases react with carbon disulphide in a manner similar to alkali hydroxides, giving xanthates. In a preliminary note, the author describes the preparation of the xanthates of quaternary ammonium, sulphine, and iodonium bases, giving some quantitative details of their properties. Tetramethylammonium hydroxide was dissolved in ethyl alcohol, and carbon disulphide added. On evaporation, the *xanthate* is obtained in yellow, hygroscopic needles, soluble in ether and acetone. With propyl alcohol, the corresponding xanthate is obtained in plates.

Phenyltrimethylammonium ethyl- and propyl-xanthates were prepared similarly, crystallising in needles. Solutions were obtained giving xanthate reactions by adding disulphide to alcoholic solutions of methylpyridinium hydroxide and methylveratrinium hydroxide.

Triethylsulphine hydroxide was dissolved in ethyl, propyl, and isobutyl alcohols. On treatment with carbon disulphide and evaporation, the corresponding *xanthates* were obtained in yellow needles soluble in water.

Diphenyliodonium hydroxide gives a *xanthate* crystallising in brilliant needles, only slightly soluble in water, alcohol, and ether.

By similar methods, *methylstibonium ethylxanthate* (colourless crystals) and *ethylmercury ethylxanthate* were prepared.

W. S. M.

Constitution of Methyloxaluric Acid. ROBERT BEHREND (*Ber.*, 1919, 52, [B], 424—426).—Only one of the two possible methyloxaluric acids is known, but its constitution has not been determined hitherto (compare Henkel, A., 1911, i, 159). Its ethyl ester, flat prisms, m. p. 144—146°, has now been heated with acetyl chloride in a sealed tube at 120—130°, and the following products have been isolated and fully identified: (a) much methylparabanic acid, (b) a small quantity of the acetyl derivative of this, and

(c) a little acetoxamethane. The last substance gives the clue to the constitution of the methyloxaluric acid, for it may be supposed to be formed according to the equation $\text{NHMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{CO}_2\text{Et} + \text{AcCl} = \text{NHAc}\cdot\text{CO}\cdot\text{CO}_2\text{Et} + \text{CH}_3\text{N}\cdot\text{CO} + \text{HCl}$. J. C. W.

Action of Halogenates and Hypohalogenites on Mercury Fulminate. A. LANGHANS (*J. pr. Chem.*, 1918, [ii], 98, 255—314).—The action of halogenates and hypohalogenites on mercury fulminate has been studied under various conditions; more definite quantitative data are promised in a subsequent paper, but the results already obtained are considered to furnish further evidence for the oxime structure for fulminic acid.

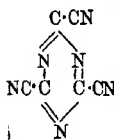
The action of potassium chlorate and potassium bromate solutions on mercury fulminate in the presence of hydrochloric acid depends greatly on the conditions of the experiment, and the original memoir must be consulted for details. Generally, it may be said that bromate acts more energetically than chlorate, and that for the production of the maximum amount of blue, oily product a definite relationship between the concentrations of hydrochloric acid and bromate must be maintained, and that the quantity of mercury fulminate is definitely related to that of the other reagents.

Mercury fulminate is decomposed by potassium hypochlorite solution, yielding chiefly mercuric oxide, which is only produced in small amount by hypobromite or hypoiodite. The action of potassium hypobromite yields varying products, according to experimental conditions, a summary of which is impossible until more exact data have been obtained; the most remarkable product is a deep blue oil, which is best obtained by the gradual addition of moist mercury fulminate to a solution of bromine in 10% potassium hydroxide, 7—8 c.c. of bromine being used for each 10 grams of potassium hydroxide; it has D 2.6844 or 2.6852, and is unstable towards light, but more stable in the dark. It consists in all probability of *tribromonitrosomethane*. It decomposes when distilled under ordinary pressure, evolving brown vapours and yielding distillates, which generally crystallise after a time. It yields crystalline products when treated with the following reagents: sodium sulphite or sodium hydrogen sulphite (colourless leaflets, m. p. 91—92° [uncorr.] after softening at 89°); sodium thiosulphate; potassium cyanide (m. p. 55°); ammonium persulphate (m. p. 68°); silver nitrate (colourless leaflets, m. p. 67°); phenylhydrazine; furfuraldehyde (m. p. above 200°); benzoyl peroxide (colourless needles); hexamethylenetetramine (yellow or white solid, m. p.'s 95° and 137° respectively, according to conditions of experiment); benzenesulphonic acid; picric acid; sodium xanthogenate; glycine (m. p. 65°). The blue compound is not formed when bromine acts on mercury fulminate in the presence of acetic anhydride, glacial acetic acid, or pyridine.

A sensitive method for the detection of mercury fulminate in fusc compositions is founded on the production of the blue oil.

H. W.

Simple Cyanic and Cyanuric Compounds. I. Hexacyanogen [Cyanuric Cyanide]. ERWIN OTT (*Ber.*, 1919, 52, [B], 656—665).—*Hexacyanogen* (annexed formula) is obtained by heating a mixture of cyanuric tricarboxylamide and phosphoric oxide in a vacuum rapidly to 210—220°, and finally to about 250°. The yield is about 17%.



The substance forms monoclinic crystals ($a:b:c = 0.9233:1:1.0688$, $\beta = 90^\circ 26'$), has m. p. 119° , b. p. 262° (corr.)/771 mm., $119^\circ/0.5-1$ mm. It separates from benzene + $1C_6H_6$. When the vapour is led over a strongly heated platinum wire, it is quantitatively depolymerised to dicyanogen. It is very sensitive to moisture. It slowly dissolves in water at 0° , and two cyanogen groups are rapidly eliminated in the form of hydrogen cyanide, whilst the third cyanogen group is removed at a slightly higher temperature, cyanuric acid being formed. In virtue of the three conjugated double linkings, it seems probable that water is first added and hydrogen cyanide subsequently eliminated from the hydroxynitrile, thus formed. With methyl alcohol, reaction proceeds more slowly, and can be arrested by suitable adjustment of experimental conditions at any of the three stages theoretically possible. There are thus obtained: (1) the *monomethoxydinitrile*, $OMe \cdot C_3N_3(CN)_2$, colourless leaflets; m. p. 86.5° , (2) the *dimethoxymononitrile*, prisms, m. p. 21° , and (3) trimethyl cyanurate, m. p. 135° . A solution of hexacyanogen in carbon tetrachloride does not visibly react with chlorine even in the presence of iodine, but the odour of cyanuric chloride shows some action to occur; it also appears to be indifferent to hydrogen chloride.

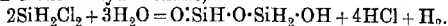
H. W.

Silicon Hydrides. VI. Chlorination and Methylation of Monosilane. ALFRED STOCK and CARL SOMIESKI (*Ber.*, 1919, 52, [B], 695—724. Compare A., 1916, ii, 319; 1917, ii, 110, 111, 353, 361).—Whilst monosilane does not react with hydrogen chloride in the absence of a catalyst at 200° , reaction occurs slowly in the presence of aluminium chloride at the ordinary temperature, and with reasonable rapidity at 100° ; when the gases are used in molar proportions, the chief product is monochlorosilane, whilst with the double proportion of hydrogen chloride, *dichlorosilane* is chiefly formed, the action in this respect differing somewhat considerably from that with hydrogen bromide.

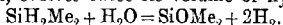
Chloromonosilane is a non-spontaneously inflammable gas, m. p. -118° , b. p. -30.5° , $D_{-118^\circ} 1.145$ (as liquid). It is immediately decomposed by water, yielding disiloxane; protracted action of water causes hydrolysis with evolution of hydrogen. It reacts with gaseous zinc methyl, yielding exclusively *methylmonosilane*, SiH_3Me , b. p. -57° , m. p. -156.5° , which is scarcely attacked by water in the absence of alkali, but is slowly decomposed by alkali in accordance with the equation $SiH_3Me + 2H_2O = [Si(OH)Me]_2 +$

3H_2 . Further chlorination of methylsilane by means of hydrogen chloride and aluminium chloride leads to the production of *methylchloromonosilane* and *methyldichloromonosilane*, which can be separated by protracted fractional distillation. The former is a colourless gas, m. p. 134° , b. p. ca. $+7^\circ$, D_{-8}° 0.935 (as liquid), which is very sensitive to moisture; evidence that the chlorine atom is attached to silicon is afforded by converting it into dimethylsilane by the action of zinc methyl, the product being identical with that prepared from dichlorosilane. Dichloromethylmonosilane was isolated in approximately pure condition.

Dichloromonosilane is obtained as a by-product in the preparation of the monohalogen derivative by further chlorination of chloromonosilane by aluminium chloride and hydrogen chloride, and by the action of hydrogen chloride (2 mols.) on monosilane (1 mol.); in the latter case, the main product is the dichloro-derivative mixed with a little monochloro-product and unchanged hydrogen chloride and very little trichloromonosilane. It has n. p. -122° , b. p. 8.5° , and is particularly sensitive to moisture and fat. With water, it immediately yields prosiloxane, $\text{SiH}_2(\text{O})_2$, and then 1-oxo-2-oxydisiloxane,



It is converted by thorough treatment with gaseous zinc methyl into dimethylmonosilane, SiH_2Me_2 , m. p. -150° , b. p. -20° , which, with alkali, evolves twice its volume of hydrogen,



The dimethylprosilo-xane is soluble in an excess of alkali, probably yielding $\text{SiMe}_2(\text{ONa})_2$; acids precipitate an oil from this solution which slowly becomes partly solid, and consists of a mixture of SiMe_2O , $\text{SiMe}_2(\text{OH})_2$, and their condensation and polymerisation products.

It is noticeable that the displacement of hydrogen by chlorine in silicon derivatives has much less influence in raising the boiling and melting points than with derivatives of carbon. H. W.

Nitration of *tert*-Butylbenzene. D. F. DU TOIT MALHERBE (*Ber.*, 1919, 52, [B], 319—324).—When *tert*-butylbenzene is left with nitric acid (D_{15}°), it is almost entirely converted into *p*-nitro-*tert*-butylbenzene, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CMe}_3$, an oil which does not crystallise in a freezing mixture, having b. p. $142\text{--}143^\circ/17\text{ mm.}$, whilst a dinitro-derivative, pale yellow prisms, m. p. $61\text{--}62^\circ$, b. p. $185^\circ/15\text{ mm.}$, is formed at 60° (Baur, *Ann.*, 1894, i, 445).

The constitution of the mono-nitro-compound does not agree with Senkowski's statements (*Ann.*, 1890, 1296). It has been proved as follows: (a) oxidation with dilute nitric acid at 130° to *p*-nitrobenzoic acid; (b) reduction to *p*-*tert*-butylaniline, and conversion into its acetyl, benzoyl, and dimethyl derivatives, and into *p*-*tert*-butylphenol; (c) reduction by sodium methoxide solution to *p*-azoxy-*tert*-butylbenzene, pale yellow leaflets, m. p. 138° ; (d) reduction to *p*-azo-*tert*-butylbenzene, orange-red needles, m. p. 183° , and the hydrazo-compound by means of aqueous-alcoholic

potassium hydroxide and zinc dust; (e) the semidine transformation of the hydrazo-derivative, by means of alcoholic stannous chloride, into 6-amino-3:4'-di-tert.-butyldiphenylamine,

$\text{CMe}_3\cdot\text{C}_6\text{H}_3(\text{NH}_2)\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CMe}_3$,
white leaflets, m. p. 100—101°. As an *o*-aminodiphenylamine, the latter base reacts with benzil to form a stilbazonium compound, $\text{C}_{24}\text{H}_{20}\text{ON}_2$, greenish-yellow needles, m. p. 165—167° (Taüber, A., 1892, 853), and with benzaldehyde to give a benzoyl compound, $\text{C}_{27}\text{H}_{22}\text{N}_2$, slender, yellow needles, m. p. 126—127° (*ibid.*).
J. C. W.

New Compounds of Glutamic Acid. PETER BERGELL (*Zeitsch. physiol. Chem.*, 1919, 104, 182—188).— *β -Naphthalenesulphonylglutamic acid*, $\text{C}_{10}\text{H}_7\cdot\text{SO}_2\cdot\text{NH}\cdot\text{CH}(\text{CO}_2\text{H})\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{H}$, crystallises in microscopic needles from water, m. p. 165° (uncorr.).
Toluenesulphonylglutamic acid,

$\text{C}_7\text{H}_7\cdot\text{SO}_2\cdot\text{NH}\cdot\text{CH}(\text{CO}_2\text{H})\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{H}$,
forms woolly masses of soft, short needles, m. p. 115—117° (uncorr.). The presence of 1% of glutamic acid or glycine in urine may be detected by the isolation of their β -naphthalenesulphonyl derivatives.
J. C. D.

Formation of Diphenyl by the Action of Cupric Salts on Organometallic Compounds of Magnesium. JACOB KRIZEWSKY and EUSTACE EBENEZER TURNER (T., 1919, 114, 559—561).

Transformation of Quaternary Ammonium Salts into Tertiary Amines with Sodium Ethoxide. D. VORLÄNDER and ELISABETH SPRECKELS (*Ber.*, 1919, 52, [B], 309—311).—Aromatic primary amines can be readily converted into a mixture of the dimethyl derivatives and the corresponding quaternary salts by treatment with an excess of methyl sulphate and alkali. A convenient process for transforming the quaternary salts into the tertiary bases has now been found. The crude product is saturated with hydrochloric acid, evaporated to dryness, and the mixed salts are boiled under reflux with a solution of sodium (two or three equivalents) in alcohol (50—100 parts) for three to five hours. From 85 to 95% of the quaternary salt is converted into the tertiary amine.

The process has not been fully tested in the case of aliphatic bases, but more concentrated solutions of sodium ethoxide, or perhaps amyloxide, appear to be necessary.
J. C. W.

Oxidation of *o*-Tolytrimethylammonium Salts to *o*-Benzobetaine. D. VORLÄNDER and FRANZ JANECKE (*Ber.*, 1919, 52, [B], 311—314).—The oxidation of *o*-tolytrimethylammonium methyl sulphate (Ullmann, A., 1903, i, 395) to *o*-benzobetaine (Willstätter, A., 1904, i, 235) by means of permanganate is described. In addition to the hydriodide, aurichloride, and free base already obtained by Willstätter, the authors have prepared the hydro-

chloride, $C_{10}H_{14}O_2NCl \cdot H_2O$, jagged leaflets, m. p. $170-176^\circ$. When boiled with a solution of sodium ethoxide, the base deposits the sodium salt of *N*-dimethylantranilic acid in felted needles. The free acid corresponds with Willstätter's description (*ibid.*), and forms a *hydriodide*, m. p. 180° (decomp.), a *periodide*, m. p. 163° (decomp.), and a *platinichloride*, m. p. 198° (decomp.).

J. C. W.

Nitration of Benzotrichloride. ELISABETH SPRECKELS (*Ber.*, 1919, **52**, [B], 315-319).—Under the usual conditions of nitration, benzotrichloride yields nitrobenzoic acids, but if treated with a solution of nitrogen pentoxide in carbon tetrachloride at -10° , a mixture of nitrobenzotrichlorides is formed almost free from nitrobenzoic acids and unchanged material. About 80% of the mixture has b. p. $150-153^\circ/18$ mm. It is fairly stable towards water and cold dilute alkalis, much more so, in fact, than benzotrichloride itself, neither does it readily change into the nitrobenzoic acids in contact with cold, concentrated nitric acid. It is not, therefore, the precursor of the nitrobenzoic acids formed under the usual conditions.

The proportions of the isomerides in the mixture have been determined approximately by boiling with barium hydroxide and separating the barium salts of the nitrobenzoic acids. The main product is *m*-nitrobenzotrichloride, with about one-fifth of its weight of the *para*-compound, which is much more than benzoic acid yields. There is also a small quantity of the *ortho*-compound in the mixture.

J. C. W.

Phenylcarbamic Acid and its Homologues. F. E. C. SCHEFFER (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 664-677).—The compound formed between aniline and carbon dioxide under pressure at low temperatures was examined by Ditte many years ago (A., 1888, 49), and was found to contain the constituents in equimolecular proportions. This composition has now been confirmed and the conditions of its existence established. Within the limits of temperature and pressure of the experiments, four phases are possible—the solid compound, two liquids, and vapour. The four three-phase *P-T* curves have been determined and the point of intersection, the quadruple point, found at 18° with a pressure of 52.0 atm. The critical end-point lies at 37° , that is, 6° and about 7 atm. higher than the critical point of carbon dioxide.

Similar compounds are formed between carbon dioxide and the three toluidines. The quadruple points of the three compounds are as follows: *o*-toluidine, -7.5° , 27.5 atm.; *m*-toluidine, 6.3° , 39.2 atm.; *p*-toluidine, (1) 31.5° , 70 atm., (2) 29.7° , 44 atm. In the last case, there are two quadruple points; the first has the compound as the solid phase, whilst the second has *p*-toluidine and the compound both present as solid phases in equilibrium with one liquid and vapour. Whilst *o*-toluidine has the lowest quadruple

point, *m*-toluidine has the lowest melting point, but otherwise the quadruple and melting points follow the same order. The critical end-points lie close together, and the three-phase curves L_1L_2G (two liquids and vapour) are nearly coincident.

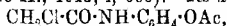
All the compounds contain base and carbon dioxide in molecular proportions, and are to be regarded as carbamic acids.

E. H. R.

Preparation of Phenol. H. H. Dow (U.S. Pat. 1274394).—Bromobenzene is converted into phenol by heating with a dilute alkali hydroxide solution in closed vessels under a pressure of 20 atmospheres. [See *J. Soc. Chem. Ind.*, June.] G. F. M.

Some Aromatic Amines and Chloroacetyl Derivatives. WALTER A. JACOBS, MICHAEL HEIDELBERGER, and IDA P. ROLF (*J. Amer. Chem. Soc.*, 1919, **41**, 458—474).—The compounds described in this communication are intermediate products in the preparation of several aromatic arsenic derivatives, which will be dealt with in a future series of papers.

An improved method for preparing *o*-chloroacetylaminophenol is described (compare A., 1916, i, 668). Its *acetate*,



obtained by the action of acetic anhydride and a drop of sulphuric acid, has m. p. 113·5—114·5°.

4-Chloroacetylaminophenol, rhombic plates, m. p. 154—155°, and the more soluble 6-chloroacetylaminophenol, silky needles, m. p. 151—152·5°, are prepared from the aminocresols by the new way (A., 1917, i, 552).

1-Chloroacetylaminophenol forms very pale yellow, nacreous plates, m. p. 192—193° (decomp.), and 4-chloroacetylaminophenol crystallises in long, faintly purple, silky needles, m. p. 199·5—201·5°.

4:6-Dichloro-3-acetylaminophenol is obtained in silky needles, m. p. 233—236°, by chlorinating *m*-acetylaminophenol in acetic acid solution, and is hydrolysed by boiling with hydrochloric acid to 4:6-dichloro-3-aminophenol, large, striated prisms, m. p. 135—136°, which is converted into 4:6-dichloro-3-chloroacetylaminophenol, slender, interlaced needles, m. p. 185·5—186·5°. The 4:6-dichloro-3-acetylaminophenol is also methylated by means of methyl sulphate, and the 4:6-dichloro-3-acetanisidide, tufts of delicate needles, m. p. 157·5—159°, is hydrolysed to 4:6-dichloro-3-anisidine, which crystallises in creamy, rhombic prisms, m. p. 50·5—51·5° (corr.). The constitution of the compounds of this series is revealed by converting the latter base, by the diazo-reaction and application of methyl sulphate, into 4:6-dichloro-1:3-dimethoxybenzene (Auwers and Pohl, A., 1914, i, 981).

If the chlorination of *m*-acetylaminophenol is carried out without the precaution of shaking the acetic acid mixture, a good deal of 2:4:6-trichloro-3-acetylaminophenol is formed. This separates when the dilute acetic acid mother liquors from the dichloro-com-

pound are further diluted, and it crystallises in rhombic plates with $0\cdot5\text{H}_2\text{O}$, or anhydrous needles, m. p. $185\text{--}186\cdot5^\circ$.

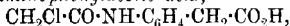
6-Bromo-3-acetylaminophenol is prepared by direct bromination and hydrolysed to 6-bromo-3-aminophenol (compare Heller, A., 1909, i, 568). 6-Bromo-3-chloroacetylaminophenol crystallises in rhombs, m. p. $191\text{--}193^\circ$.

m-Acetylaminophenol is also boiled with chloroacetic acid and concentrated sodium hydroxide, and thus converted into *m*-acetylaminophenoxyacetic acid, $\text{NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, which crystallises from water in slender needles with $1\text{H}_2\text{O}$, or from acetic acid in spherules, m. p. $170\cdot5\text{--}172\cdot5^\circ$. This is hydrolysed to *m*-aminophenoxyacetic acid (A., 1917, i, 695), and then converted into *m*-chloroacetylaminophenoxyacetic acid, spherules, m. p. $159\text{--}160^\circ$ (clear at 162°).

Considerable quantities of 4-aminoguaiacol were required for the preparation of catechol derivatives. This is obtained by coupling diazotised sulphanilic acid with guaiacol and reducing the crude dye with hydrogen sulphide in ammoniacal solution. *p*-Sulphobenzeneazoguaiacol crystallises from water in glistening, green needles and long, thin plates with $1\text{H}_2\text{O}$, decomp. above 220° . 4-Aminoguaiacol is hydrolysed by means of hydrobromic acid to the hydrobromide (flat needles or plates, decomp. $255\text{--}260^\circ$) of 4-aminocatechol, which crystallises from a mixture of alcohol and benzene in grey plates and clusters of short prisms, m. p. $124\text{--}125^\circ$ (decomp., purple residue). In the isolation and filtration of the base, air must be excluded as far as possible by a current of carbon dioxide. 4-Chloroacetylaminocatechol, $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_3(\text{OH})_2$, forms slender needles, m. p. $156\text{--}157\cdot5^\circ$.

p-Chloroacetylaminocatechol crystallises as a woolly mass of needles from alcohol or leafy aggregates of plates from toluene, m. p. $152\text{--}153^\circ$ (corr.).

p-Chloroacetylaminophenylacetic acid,



forms a snowy mass of needles, m. p. $158\text{--}160^\circ$.

Ethyl chloroacetylthranilate, $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Et}$, crystallises in glistening needles, m. p. $79\cdot5\text{--}80^\circ$ (corr.), and changes into ethyl iodoacetylthranilate, transparent prisms, m. p. $78\cdot5\text{--}79^\circ$ (corr.), when warmed with a solution of sodium iodide in acetone. *o*-Methylaminobenzoic acid yields chloroacetyl-N-methylthranilic acid, $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, colourless spears, m. p. $167\text{--}168^\circ$ (corr.), the ethyl ester of which forms stout prisms, m. p. $50\text{--}51^\circ$ (corr.).

Sodium sulphanilate gives rise to sodium chloroacetylsulphanilate, $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{Na}$, which crystallises in hair-like masses of needles, decomposing somewhat when dried at 100° .

3-Amino-*o*-phenolsulphonic acid, prepared by heating *m*-aminophenol with concentrated sulphuric acid at 100° , yields 3-chloroacetyl-amino-*o*-phenolsulphonic acid, minute plates and flat needles, not molten at 275° , the sodium salt of which crystallises as a voluminous mass of small needles with $0\cdot5\text{H}_2\text{O}$.

Improvements in the preparation of chloroacetomethylamide and chloroacetopiperidide are described (compare A., 1915, i, 668). *Chloroaceto-n-propylamide*, $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NHPr}^3$, has b. p. 105–106°/10.5 mm. (corr.), and forms a *hexamethylenetetraminium* salt, in stout, hexagonal plates, m. p. 147–149°.

Ethylcarbamide yields *chloroacetylethylcarbamide*,
 $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NHEt}$,
 in long needles, m. p. 141.5–142.5° (corr.). J. C. W.

Catalytic Preparation of the Aminophenols and the Phenylenediamines. O. W. BROWN and L. L. CARRICK (*J. Amer. Chem. Soc.*, 1919, **41**, 436–440).—Mignonac (*Bull. Soc. chim.*, 1910, [iv], **7**, 270) described the reduction of the nitrophenols by passing a mixture of their vapours and hydrogen over nickel at 160–190°, but found that the production of the aminophenols was accompanied by the formation of ammonia, phenol, and aniline. This work is confirmed, and it is also reported that nickel is not so active when deposited on pumice as otherwise.

With finely divided copper, deposited on small pieces of pumice, the reduction is more efficient than with nickel, there being no by-products. Thus *o*- or *p*-nitrophenol and hydrogen passed over copper at 210–315° (best, 265°) give practically quantitative yields of the pure white aminophenols, the more volatile product, of course, reacting more quickly. The *o*-aminophenol is obtained in plates when copper is used, but when reduced nickel is employed, it is formed in long needles with the same m. p. (170°), especially at the higher ranges of temperature.

The nitroanilines, and especially *m*-dinitrobenzene, may be reduced in the same way to the phenylenediamines, but the process is too slow (owing to the slight volatility of the compounds) to be of much practical value, the only advantage being the high degree of purity of the products. J. C. W.

Transformation of Phenyl Allyl Ethers into the Isomeric Allylphenols. II. L. CLAISEN (*Annalen*, 1919, **418**, 69–120. Compare A., 1912, i, 965; 1913, i, 1175).—I. *Mono-, Di-, and Tri-allylation of Phenol* [with O. EISLEB and F. KREMERS].—*o*-Allylphenol, b. p. 220°/760 mm. or 99°/12 mm., D_4^{20} 1.0255, is obtained (1) by heating phenyl allyl ether in an atmosphere of carbon dioxide until the temperature is about 220°, heating for about six hours being necessary, (2) by heating 4-allyloxybenzoic acid with quinoline at 170°, and finally at the b. p. of the solution, (3) by heating 3-allylsalicylic acid with dimethylaniline slowly to the b. p. of the solution, (4) by boiling a mixture of methyl 3-allylsalicylate and aniline for four hours, and (5) least satisfactorily from 2-allyloxybenzoic acid. In the first method, a small quantity of 1-methylcoumaran is formed, which is removed by extraction with light petroleum after basifying the reaction product with 20% sodium hydroxide. Attempts to accelerate the transformation of phenyl allyl ether into *o*-allylphenol by catalysts were unsuccessful; alkalis had no effect, and acids only increased the amount of methyl-

coumaran, the addition of pyridine hydrochloride, for example, resulting in the production of this compound in 60% yield.

The position of the allyl group in *o*-allylphenol is proved (1) by heating with methyl-alcoholic potassium hydroxide, whereby Pauly and Buttlar's *o*-propenylphenol is obtained, (2) by heating the methyl ether of the allylphenol with potassium hydroxide and oxidising the resulting *o*-propenylphenyl methyl ether, whereby *o*-methoxybenzoic acid is obtained, and (3) by coupling allylphenol with benzenediazonium chloride, the product being identical with the 4-benzeneazo-2-allylphenol obtained by the transformation of 4-benzeneazophenyl allyl ether (*loc. cit.*).

o-Allylphenol forms a *phenylcarbamate*,
 $\text{C}_3\text{H}_5\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CO}\cdot\text{NHPh}$,

colourless needles, m. p. 106—106.5°, methyl ether (*o*-*esdrugale*), b. p. 207°/761 mm. or 86—87°/12 mm., D_{15}^{25} 0.9770 (the *ozonide* of which is very explosive and yields *o*-methoxyphenylacetaldehyde by treatment with glacial acetic acid and zinc dust), and *acetate*, b. p. 238.5—239°/757 mm. or 117—118°/15 mm.; the last derivative forms an oily *dibromide*, which is converted into 1-methyl-coumarone by boiling with methyl-alcoholic potassium hydroxide.

To the list of substitution products of *o*-allylphenol already described (*loc. cit.*) is to be added 4:6-dichloro-*o*-allylphenol, b. p. 264°, D_{15}^{25} 1.288, which is very easily obtained by heating 3:5-dichloro-2-allyloxybenzoic acid, needles, m. p. 118° (decomp.); the methyl ester of this acid, $\text{C}_5\text{H}_5\cdot\text{O}\cdot\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{CO}_2\text{Me}$, b. p. 160°/10 mm., is prepared by boiling methyl 3:5-dichlorosalicylate in methyl ethyl ketone solution with allyl bromide and potassium carbonate.

o-Propylphenol is obtained by reducing *o*-allylphenol by the Paal-Skita method, and also by reducing 3-allylsalicylic acid in a similar manner and heating the resulting 3-propylsalicylic acid, m. p. 91.5° (Spica gives 93—94°), with dimethylaniline at the b. p. of the solution until the evolution of carbon dioxide ceases. 2-Acetoxy-3-propylbenzoic acid (3-propylaspirin) crystallises in needles, m. p. 97—97.5°.

2:6-Diallylphenol, b. p. 256—257°/770 mm. (slight decomp.; in carbon dioxide) or 130°/15 mm., has D_{15}^{25} 0.9920, not 0.9905, as stated previously (*loc. cit.*). It is readily obtained by heating *o*-allylphenyl allyl ether, b. p. 104—105°/10 mm., D_{15}^{25} 0.9675 (prepared from *o*-allylphenol in acetone solution, allyl bromide, and potassium carbonate), for ten minutes in an atmosphere of carbon dioxide while the temperature rises from 235° to 256°, or, better, with half its weight of diethylaniline for thirty minutes while the temperature increases from 225° to 237°. It forms a *phenylcarbamate*, needles, m. p. 141—142°. Its constitution is definitely proved by the production of the compound by heating 4-hydroxy-3:5-diallylbenzoic acid (*loc. cit.*) with dimethylaniline at the b. p. for one to one and a-half hours. By hydrogenation in alcoholic solution, 2:6-diallylphenol yields 2:6-dipropylphenol, b. p. 256°/764 mm., m. p. 28° (*phenylcarbamate*, needles, m. p. 125°).

4-Allylphenol and 2:4-diallylphenol are not produced by the transformation of phenyl allyl ether and *o*-allylphenyl allyl ether respectively. The latter, b. p. 266°–268°/750 mm. (*phenylcarbamate*, prisms, m. p. 88–88.5°), is obtained indirectly by heating 3:5-diallylsalicylic acid (*loc. cit.*) with dimethylaniline at the b. p. for thirty to forty-five minutes. 3:5-Dipropylsalicylic acid, needles, m. p. 100–100.5°, obtained by reducing 3:5-diallylsalicylic acid in alcoholic solution by the Paal-Skita method, is converted by boiling with dimethylaniline into 2:4-dipropylphenol, b. p. 263°/747 mm. or 130°/11 mm., D_{15}^{25} 0.9350 (*phenylcarbamate*, needles, m. p. 131°).

2:6-Diallylphenyl allyl ether, b. p. 132.5–134°/11 mm., D_{15}^{25} 0.9548, is prepared by heating an alcoholic solution of 2:6-diallylphenol with allyl bromide and potassium carbonate on the water-bath for ten hours. When it is heated in a current of carbon dioxide until the temperature rises from about 250° to about 290°, or, better, when it is boiled with half its weight of diethylaniline for fifteen minutes until the temperature rises from 225° to 248°, it is transformed into 2:4:6-triallylphenol (*loc. cit.*), b. p. 293–295°/760 mm. or 158–159°/14 mm., D_{15}^{25} 0.9785.

The influence of the b. p. of an allyl ether on the rapidity of its transformation into the allylphenol (*loc. cit.*) is well illustrated by the production of *o*-allylphenol, 2:6-diallylphenol, and 2:4:6-triallylphenol from the respective allyl ethers. The first reaction requires about six hours, the second proceeds much more rapidly, and the third almost instantly. It is to be noted, however, that the quantity of resinous matter produced is greater the higher is the temperature of transformation. The formation of this by-product is greatly diminished by heating in an atmosphere of hydrogen or carbon dioxide, or, best of all, by boiling the ether with dimethyl- or diethyl-aniline. The basic nature of this solvent appears to be of influence, since an indifferent, non-basic solvent of similar b. p. effects a much less satisfactory transformation.

cycloHexanol allyl ether, b. p. 169–172°/740 mm., D_{15}^{25} 0.8960, obtained by warming a benzene solution of cyclohexanol with sodium for one day and then boiling with allyl bromide, cannot be transformed into allylcyclohexanol.

II. Nitroso- and Amino-derivatives of Monoallylphenol and Diallylphenol [with F. KREMERS].—These two phenols yield nitroso-derivatives very smoothly. 4-Nitroso-2-allylphenol (2-allyl-p-benzoquinone-4-oxime), $\text{OH}\cdot\text{N}\cdot\text{C}_6\text{H}_3(\text{C}_3\text{H}_5)_2\text{O}$, leaflets, m. p. 100–101° (decomp.), is obtained in the form of its sodium salt, garnet needles, by keeping a mixture of *o*-allylphenol, amyl nitrite, and concentrated methylalcoholic sodium methoxide solution for one day at the ordinary temperature and one day at 0°. The sodium salt, by warming on the water-bath for ten minutes with zinc dust and a cold, saturated solution of ammonium carbonate, or by treatment below 30° with hydrogen sulphide, a solution of ammonium chloride containing 25% aqueous ammonia being used as solvent,

is reduced to 4-amino-2-allylphenol, leaflets, m. p. 113·5—114°, the *N*-acetyl derivative of which forms leaflets, m. p. 93°.

4-Nitroso-2:6-diallylphenol (2:6-diallyl-*p*-benzoquinone-4-oxime), leaflets, m. p. 142—143°, obtained in a similar manner from 2:6-diallylphenol (a sodium salt is not precipitated in this case), yields 4-amino-2:6-diallylphenol, flattened prisms, m. p. 78·5°, by reduction with ammonium sulphide and concentrated aqueous ammonia.

III. *The Allyl Ether Transformation of Aminophenols* [with F. KREMERS].—*p*-Acetylaminophenol (used in preference to *p*-aminophenol to avoid allylation at the nitrogen atom) is boiled with acetone, allyl bromide, and potassium carbonate, and the resulting *p*-acetylaminophenyl allyl ether, leaflets, m. p. 93°, is boiled with dimethylaniline for six hours in a slow current of hydrogen, whereby the 4-acetylamino-*o*-allylphenol, m. p. 93°, described above is obtained; its ethyl ether, $\text{NHAc}\cdot\text{C}_6\text{H}_3(\text{C}_3\text{H}_5)\cdot\text{OEt}$, colourless leaflets, m. p. 121·5°, shows a very slight antipyretic action in comparison with phenacetin. By treatment with fuming hydrobromic acid, 4-acetylamino-*o*-allylphenol is converted into 4-acetyl-amino-1-methylcoumaran, $\text{NHAc}\cdot\text{C}_6\text{H}_3\left\langle\begin{smallmatrix}\text{O} \\ \text{CH}_2\end{smallmatrix}\right\rangle\text{CHMe}$, colourless needles, m. p. 127—127·5°. By boiling for one hour with 10% hydrochloric acid or 25% sulphuric acid, *p*-acetylaminophenyl allyl ether is converted into the hydrochloride, leaflets, m. p. 212°, or the sulphate of *p*-aminophenyl allyl ether, both of which are very sparingly soluble in water. *p*-Aminophenyl allyl ether is converted into 4-amino-*o*-allylphenol (above) by heating with petroleum (b. p. 185°) for six hours in a current of hydrogen, and the latter into 4-amino-*o*-propenylphenol, $\text{NH}_2\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CH}\cdot\text{CHMe}$, silvery leaflets, m. p. about 172° (rapidly heated) or 168° (slowly heated), by boiling with very concentrated methyl-alcoholic potassium hydroxide in a slow current of hydrogen. The propenyl compound is more conveniently obtained by submitting 4-acetylamino-*o*-allylphenol to the same treatment.

4-Acetylamino-*o*-allylphenol is converted by boiling acetone, allyl bromide, and potassium carbonate into 4-acetylamino-*o*-allylphenyl allyl ether, colourless leaflets, m. p. 111·5—112°, which yields 4-acetylamino-2:6-diallylphenol, leaflets and needles, m. p. 83—86°, by treatment by the dimethylaniline method; from the latter, 4-amino-2:6-diallylphenol (above) is obtained, but not satisfactorily, by boiling with dilute sulphuric acid in an atmosphere of hydrogen.

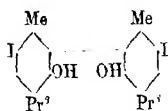
IV. *Synthesis of Eugenol* [with F. KREMERS].—Methyl guaiacol-carboxylate (3-methoxysalicylate), m. p. 66—66·5° (Fritsch gives 63°; Einhorn, 73°), is converted by boiling with methyl ethyl ketone, allyl bromide, potassium carbonate, and a little potassium iodide for seven hours into methyl 3-methoxy-2-allyloxybenzoate, b. p. 165—167°/8 mm., which yields the corresponding acid, $\text{C}_{11}\text{H}_{12}\text{O}_4$, needles, m. p. 65°, by hydrolysis with boiling 30% methyl-

alcoholic potassium hydroxide. When heated, the acid loses carbon dioxide and suffers transformation, yielding *o*-eugenol almost exclusively, but its methyl ester is converted almost explosively at 230–240° into methyl 6-hydroxy-5-methoxy-3-allylbenzoate, needles, m. p. 55–55.5°, b. p. 173–174°/12 mm. On account of the violence of the transformation, a method of heating under diminished pressure (in this case 200°/60 mm.) was tried, and gave such satisfactory results that it is recommended for the transformation of other allyl ethers into allylphenols. On hydrolysis, the preceding ester yields 6-hydroxy-5-methoxy-3-allylbenzoic acid, prisms, m. p. 127° (hydrated, m. p. 85–88°), which is converted into eugenol by heating with dimethylaniline at 160°; the methyl ester also yields eugenol (and methylaniline) by boiling with aniline for four hours. C. S.

The Aristols and the Quantitative Estimation of Thymol.

E. MOLES and M. MARQUINA (*Anal. Fis. Quim.*, 1919, 17, 59–83).

—Aristol is obtained as a red precipitate on adding a solution of iodine in potassium iodide to an alkaline solution of thymol (Messinger and Vortmann, A., 1889, 1150). On drying, the red substance loses water and iodine and passes into a yellow powder, one molecule of aristol giving 75 molecules of water and 0.15 atom of iodine. The freshly precipitated substance appears to behave as a gel in which iodine is adsorbed. The m. p. of both forms varies between 105° and 115°. A possible quinonoid or ketone structure was tested by means of hydriodic acid and by phenylhydrazine with negative results. Determinations of the molecular weight by cryoscopic measurements in benzene and thymol show that double molecules are present in the former solvent and single in the latter, the polymerisation indicating a phenolic structure. The constitution assigned to the yellow aristol is diiododithymol (annexed formula). The following method



for the estimation of thymol is given: The thymol, dissolved in water, is added to sodium hydrogen carbonate solution. A measured quantity of standard iodine solution in excess is added, and the mixture is acidified with sulphuric or hydrochloric acid. The excess of iodine is titrated with thiosulphate solution. Over wide ranges of variation in the value of the ratios thymol:sodium hydrogen carbonate and thymol:iodine added, the mean value of the quantity of iodine consumed was 3.60 atoms per molecule of thymol. W. S. M.

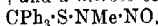
Triphenylmethyl Sulphur Compounds. D. VORLÄNDER and ERNST MITTAG (*Ber.*, 1919, 52, [B], 413–423. Compare A., 1913, i, 1335).—A poor yield of triphenylmethyl sulphide, $S(CPh_3)_2$, may be obtained by the interaction of triphenylchloromethane and alcoholic sodium sulphide or sodium triphenylmethyl sulphide, CPh_3SnA . It is a white powder, m. p. 182° (decomp.), which only

reacts with alcoholic mercuric cyanide on boiling, mercuric sulphide being formed.

When an ethereal solution of triphenylmethylthiol is treated in the cold with an equimolecular proportion of sulphuryl chloride, *triphenylmethyl thiocchloride* [*chlorothioltriphenylmethane*] is deposited in yellow prisms, m. p. 137°, according to the equation $\text{CPh}_3\cdot\text{SH} + \text{SO}_2\text{Cl}_2 = \text{CPh}_3\cdot\text{SCl} + \text{SO}_2 + \text{HCl}$. The compound is very stable towards water, but is decomposed by alkali hydroxides. The chlorine atom is readily replaced by other groups, using basic reagents, the following examples being described: (1) A solution of sodium methoxide gives *triphenylmethyl methoxyl sulphide*, $\text{CPh}_3\cdot\text{S}\cdot\text{OMe}$, needles, m. p. 124°, and sodium phenoxide forms *triphenylmethyl phenoxyl sulphide*, large prisms, m. p. 91·5°.

(2) Triphenylmethylthiol yields triphenylmethyl disulphide, $\text{CPh}_3\cdot\text{S}\cdot\text{S}\cdot\text{CPh}_3$

(*ibid.*). (3) Ammonia produces *triphenylmethyl sulphamide* [*triphenylmethylthiolamine*], $\text{CPh}_3\cdot\text{S}\cdot\text{NH}_2$, which crystallises in white rods, m. p. 126°, and forms an *acetyl* derivative, $\text{CPh}_3\cdot\text{S}\cdot\text{NHAc}$, needles, m. p. 187°, and a *benzylidene* compound, $\text{CPh}_3\cdot\text{S}\cdot\text{N}:\text{CHPh}$, yellow needles, m. p. 128°. (4) Methylamine yields *triphenylmethyl methylsulphamide* [*triphenylmethylthiolmethylamine*], leaflets, m. p. 119–120°, which forms an *acetyl* derivative, prismatic needles, m. p. 133°, and a *nitroso*-compound,

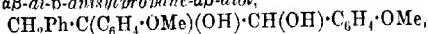


colourless crystals, m. p. 102–103° (decomp.). (5) Dimethylamine gives *triphenylmethylthioldimethylamine*, m. p. 105–108°. (6) Aniline forms *triphenylmethyl phenylsulphamide* [*triphenylmethylthiolaniline*], white tablets, m. p. 103°, and *o*-toluidine gives *triphenylmethylthiol-o-toluidine*, leaflets, m. p. 141°.

If a solution of triphenylmethylthiol in benzene is shaken with sodium nitrite solution and gradually treated with dilute sulphuric acid, or slowly mixed with liquid nitrogen trioxide or peroxide, *triphenylmethyl thionitrite*, $\text{CPh}_3\cdot\text{S}\cdot\text{NO}$, separates in green needles, m. p. 104° (decomp.). Concentrated solutions of this ester in benzene appear red in transmitted light and green by reflected light. The thiol also couples with benzenediazonium chloride in the presence of sodium hydroxide, giving *triphenylmethylthiodiazobenzene*, $\text{CPh}_3\cdot\text{S}\cdot\text{N}\cdot\text{Ph}$, yellow leaflets, m. p. 108° (decomp.).

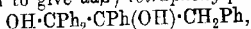
Chlorothioltrichloromethane (perchloromethyl mercaptan) condenses with benzene under the influence of aluminium chloride to form *thiobenzophenone*, Ph_3CS , a deep blue oil which yields benzophenone on boiling with alcoholic potassium hydroxide, and tetraphenylethylene on heating with copper powder. J. C. W.

Molecular Transpositions of the α -Glycols. V. The Dehydration of a Methoxy-derivative of $\alpha\beta\gamma$ -Triphenylpropane- $\alpha\beta$ -diol. A. OREKHOFF [with F. COMA Y ROCA] (*Bull. Soc. chim.*, 1919, [iv], 25, 174–179. Compare this vol., i. 205, 206).—Magnesium benzyl bromide condenses with *p*-anisoin to give *γ -phenyl- $\alpha\beta$ -di-*p*-anisylpropane- $\alpha\beta$ -diol*,



m. p. 152—153°, which when dehydrated with sulphuric acid yields *benzyl-di-p-anisylacetaldehyde*, $\text{CH}_2\text{Ph}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{OMe})_2\cdot\text{CHO}$, m. p. 71—72°, giving an *oxime*, m. p. 116—118°. The aldehyde is decomposed by alcoholic potassium hydroxide, yielding α -phenyl- $\beta\beta$ -di-p-anisylethane, m. p. 89—90°. The constitution of this latter compound was proved by its synthesis as follows: Di-p-anisyl ketone condenses with magnesium benzyl chloride, giving *phenyl-di-p-anisylethyl alcohol*, $\text{CH}_2\text{Ph}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{OMe})_2\cdot\text{OH}$, m. p. 141—142°, which when dehydrated by acetyl chloride yields *phenyl-di-p-anisylethylene*, $\text{CHPh}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{OMe})_2$, m. p. 62—63°, and this, when reduced by sodium in absolute alcohol, gives α -phenyl- $\beta\beta$ -di-p-anisylethane. W. G.

Molecular Transpositions of the α -Glycols. VI. Dehydration of $\alpha\beta\gamma$ -Tetraphenylpropane- $\alpha\beta$ -diol. A. ORÉKHOFF [with J. ZIVÉ] (*Bull. Soc. chim.*, 1919, [iv], 25, 179—182. Compare preceding abstract).—Magnesium benzyl chloride condenses with phenylbenzoin to give $\alpha\beta\gamma$ -tetraphenylpropane- $\alpha\beta$ -diol,



m. p. 141—142°, which when dehydrated with sulphuric acid yields *benzyl triphenylmethyl ketone*, $\text{CPh}_3\cdot\text{CO}\cdot\text{CH}_2\text{Ph}$, m. p. 113—113.5°; this is decomposed by alcoholic potassium hydroxide, giving triphenylmethane and potassium phenylacetate. W. G.

Molecular Transpositions of the α -Glycols. VII. The Dehydration of $\alpha\beta$ -Diphenylbutane- $\alpha\beta$ -diol and of $\alpha\beta$ -Diphenylmethylpentane- $\alpha\beta$ -diol. A. ORÉKHOFF [with J. ZIVÉ] (*Bull. Soc. chim.*, 1919, [iv], 25, 182—186. Compare preceding abstract).—By dehydrating $\alpha\beta$ -diphenylbutane- $\alpha\beta$ -diol with hot 20% sulphuric acid, Tiffeneau and Dorlencourt obtained $\alpha\alpha$ -diphenylbutaldehyde (compare A., 1906, i, 724). The authors, by using cold concentrated sulphuric acid, obtained ethyldeoxybenzoin and an *isomeric*, m. p. 32—33°, giving a *semicarbazone*, m. p. 191—192°, which was not characterised.

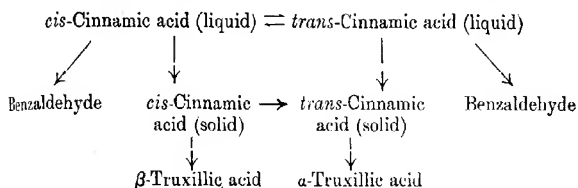
Magnesium isobutyl bromide condenses with benzoin to give $\alpha\beta$ -diphenyl- δ -methylpentane- $\alpha\beta$ -diol, m. p. 101—109°, which when dehydrated with cold concentrated sulphuric acid yields isobutyldeoxybenzoin. W. G.

Molecular Transpositions of the α -Glycols. VIII. The Constitution of the Product of Dehydration of $\alpha\beta\beta$ -Triphenylethanediol. A. ORÉKHOFF (*Bull. Soc. chim.*, 1919, [iv], 25, 186—189).—The author agrees with Kohler (compare A., 1906, i, 753) that the product of dehydration of $\alpha\beta\beta$ -triphenylethanediol is diphenylacetophenone, $\text{CHPh}_2\cdot\text{COPh}$, and not the so-called triphenylvinyl alcohol, $\text{CPh}_2\cdot\text{CPh}\cdot\text{OH}$ (compare Biltz, A., 1899, i, 439). Diphenylacetophenone condenses with magnesium phenyl bromide to give $\alpha\alpha\beta\beta$ -tetraphenylethyl alcohol, m. p. 235—236°, which is also obtained by the action of magnesium phenyl bromide on diphenylacetyl chloride. The alcohol, when dehydrated, yields tetraphenylethylene.

Diphenylacetophenone condenses with magnesium benzyl chloride to give *ααβγ-tetraphenylpropan-β-ol*, m. p. 135—136°. W. G.

Action of Light on *allo*- and *iso*-Cinnamic Acids. HANS STROBBE (*Ber.*, 1919, **52**, [B], 666—672).—Two specimens of cinnamic acid, m. p. 42°, obtained from the acids, m. p.'s 68° and 58° respectively, were exposed to bright daylight during two years; the product consisted entirely of unchanged acid and *β*-truxillic acid.

[With JUSSIÉ POGOSSIANZ].—Specimens of cinnamic acids, m. p.'s 42°, 58°, and 68° respectively, were exposed in quartz tubes to direct sunlight which was sufficiently powerful in the circumstances to cause temporary fusion, with consequent isomerisation; in each case, the product consisted chiefly of *α*-truxillic acid with little *β*-truxillic acid and minimal quantities of *trans*-cinnamic acid and benzoic acid. Reaction in the illuminated molten mass, and also in benzene solution, may be represented by the scheme:



[With EDUARD FAERBER].—The possible polymerisation of cinnamic acid by heat has been investigated either alone or in the presence of a solvent (water, naphthalene, xylene, ethylene dibromide). Polymerisation was only observed with certainty in the experiment with ethylene dibromide, when *α*-truxillic acid was formed in small amount. It is suggested that the action may be due to slight decomposition of the solvent into bromoethylene and hydrogen bromide, and the catalytic influence of the latter.

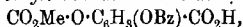
H. W.

The *O*-Benzoyl Derivatives of *β*-Resorcylic and Gentisic Acids. MAX BERGMANN and PAUL DANGSCHAT (*Ber.*, 1919, **52**, [B], 371—388).—In a recent paper (*A.*, 1918, **i**, 172), Fischer described a remarkable reaction of the acyl derivatives of some aromatic acids containing at least two hydroxyl groups in neighbouring positions, namely, the wandering of an acyl group from one place to another during hydrolysis. For example, 4-benzoyl-3-acetylprotocatechuic acid yields 3-benzoylprotocatechuic acid. In order to prove whether this phenomenon is connected with the juxtaposition of the hydroxyl groups, Fischer has suggested the present investigation on *β*-resorcylic and gentisic acids, in which the hydroxyl groups are, respectively, in *meta*- and *para*-arrangement. The authors have succeeded in isolating the two pairs of

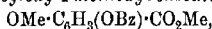
monobenzoates, but have found no indications of a tendency for the benzoyl group to wander from one position to the other.

Protocatechuic and gallic acids also only yield one carbomethoxy- or acetyl derivative, the acyl group being in the meta-position with respect to the carboxyl group. β -Resorcylic and gentisic acids yield *o*-acyloxy-compounds as well as meta- or para-derivatives.

2-Benzoyloxy-4-methylcarbonatobenzoic acid,



is obtained in long, thin needles, m. p. 148—149° (corr.), by the action of benzoyl chloride on carbomethoxyresorcylic acid (Fischer, A., 1909, i, 161), and is hydrolysed by means of *N*-ammonia solution to *4-hydroxy-2-benzoyloxybenzoic acid*, which crystallises in concentric groups of needles, m. p. 160—161° (corr.). When treated with an excess of diazomethane in dry acetone, this acid yields *methyl 2-benzoyloxy-4-methoxybenzoate*,



which crystallises in needles or flat prisms, m. p. 69—70°, and is hydrolysed by dilute aqueous-alcoholic sodium hydroxide to *4-methoxysalicylic acid*, m. p. 161° (corr.) (compare Tiemann and Parrisius, A., 1881, 270). The last compound affords the clue to the constitution of the benzoyloxy-acids.

2:4-Diacetoxybenzoic acid, well-developed, microscopic prisms, m. p. 136—138°, is obtained by heating β -resorcylic acid with acetic anhydride and zinc chloride, and is partly hydrolysed by dilute sodium hydroxide at 0° to *4-hydroxy-2-acetoxybenzoic acid*, which crystallises in lanceolate leaflets, m. p. 167—168° (corr.). This acid yields *methyl 2-acetoxy-4-methoxybenzoate*, m. p. 56—57°, on treatment with diazomethane, and this ester may be hydrolysed to *4-methoxysalicylic acid*. The acid also gives *4-benzoyloxy-2-acetoxybenzoic acid*, flat needles or prisms, m. p. 148—149° (corr.), when treated with benzoyl chloride and pyridine, and this is partly hydrolysed by a mixture of acetic and hydrochloric acids to *2-hydroxy-4-benzoyloxybenzoic acid*, needles, m. p. 193—194° (corr.). Treatment with diazomethane gives *methyl 4-benzoyloxy-2-methoxybenzoate*, m. p. 78—80°, which is hydrolysed by dilute aqueous-alcoholic sodium hydroxide to Fischer and Pfeffer's *4-hydroxy-2-methoxybenzoic acid*, decomp. 187—189° (corr.) (A., 1912, i, 559).

2-Benzoyloxy-5-methylcarbonatobenzoic acid, long, flat needles, m. p. 148—149° (corr.), is obtained from carbomethoxygentisic acid (A., 1909, i, 161) and hydrolysed by *N*-ammonia solution to *5-hydroxy-2-benzoyloxybenzoic acid*, which crystallises in microscopic leaflets, m. p. 211—212° (corr.). When treated with diazomethane, this yields *methyl 2-benzoyloxy-5-methoxybenzoic acid*, stout, quadratic plates, m. p. 106—107° (corr.), which gives the known *5-methoxysalicylic acid*, m. p. 145—146° (corr.), on hydrolysis (Tiemann and Müller, A., 1882, 52). A characteristic difference between this acid and the isomeric *5-hydroxy-2-methoxybenzoic acid*, m. p. 155—156° (Fischer and Pfeffer, *loc. cit.*), is that the

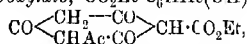
former gives a deep blue colour with ferric chloride and the latter only a grey colour.

5-Hydroxy-2-acetoxybenzoic acid, twinned prisms, m. p. 171—173° (corr.), is obtained by the partial hydrolysis of diacetyl-gentisic acid (Hemmelmeyer, A., 1909, i, 387) with *N*-ammonia in an atmosphere of hydrogen, and is converted by diazomethane into *methyl 2-acetoxy-5-methoxybenzoate*, m. p. 45—46°, which is hydrolysed to the above 5-methoxysalicylic acid. It is also converted into *5-benzoyloxy-2-acetoxybenzoic acid*, which crystallises in microscopic, bent needles, m. p. 166—167° (corr.), and yields *2-hydroxy-5-benzoyloxybenzoic acid*, leaflets, m. p. 178—179° (corr.), on hydrolysis with a mixture of acetic and hydrochloric acids. When treated with diazomethane, the acid gives *methyl 3-benzoyloxy-2-methoxybenzoate*, m. p. 83—84°, which may be hydrolysed to 5-hydroxy-2-methoxybenzoic acid. J. C. W.

Guaiaretic Acid. J. HERZIG and F. SCHIFF (*Ber.*, 1919, 52, [B], 260).—The authors agree with Schroeter and others (this vol., i, 84) that the formula of guaiaretic acid is $C_{20}H_{24}O_4$. J. C. W.

Some Derivatives of Phloroglucinol. ADOLF SONN (*Ber.*, 1919, 52, [B], 255—259).—Mosimann and Tambor have found that acetophloroglucinol will not condense with *p*-hydroxybenzaldehyde (A., 1916, i, 822), whereas its di- and tri-methyl ethers condense readily, and Sonn has found the same indifference in the case of ethyl acetophloroglucinolcarboxylate. This is most probably due to the fact that the compounds are really derivatives of triketohexamethylene.

The above ester is obtained by boiling a solution of Jerdan's lactone (A., 1917, i, 277; 1918, i, 33) in a mixture of acetic and hydrochloric acids, carbon dioxide being evolved. *Ethyl 2-acetylphloroglucinol-4-carboxylate*, $CO_2Et \cdot C_6H(OH)_3$ or



crystallises in bundles of slender needles, m. p. 77—78°, and changes into *ethyl phloroglucinolcarboxylate* when left with 25% potassium hydroxide. This ester crystallises from water with $1H_2O$, or from alcohol in anhydrous prisms or needles, m. p. 129°.

When Jerdan's lactone is left for some time with 33% potassium hydroxide and the solution is acidified, *ethyl ω -carboxyphloracetophenonecarboxylate* [*3-carbethoxyphloracetophenoneacetic acid*], $CO_2Et \cdot C_6H(OH)_3 \cdot CO \cdot CH_2 \cdot CO_2H$, is precipitated. The acid has m. p. 160°, and changes into the above ethyl 2-acetylphloroglucinol-4-carboxylate on melting or warming with acetic anhydride.

The silver salt of Jerdan's lactone, when heated with ethyl iodide, yields *ethyl 5:7-dihydroxy-4-ethoxy-1:2-benzopyrone-6(or 8)-carboxylate*, $CO_2Et \cdot C_6H(OH)_2 \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C(OEt)} \quad \text{CH} \end{array}$ in thin, prismatic crystals, m. p. 160°.

J. C. W.

Constitution of Bile Acids. I. Cholanic, isoCholanic, and ψ -Cholanic Acids. W. BORSCHKE and EMMY ROSENKRANZ (*Ber.*, 1919, **52**, [B], 342—345).—When bilianic and isobilianic acids, $C_{21}H_{31}(CO)_2(CO_2H)_3$, are reduced by means of amalgamated zinc and hydrochloric acid, they yield cholanic and isocholelanic acids, $C_{20}H_{29}(CO)(CO_2H)_3$. The ketone group of the latter pair of isomerides therefore corresponds in position with one ketone group of the former pair, and accordingly the $-CH-OH-$ groups of deoxycholic acid and cholic acid which gave rise to these ketonic acids are identically placed. It has already been proved that the second alcoholic group of deoxycholic acid, $C_{24}H_{40}O_4$, is identical with a second group in cholic acid, $C_{24}H_{40}O_5$, the evidence being the great similarity between the ketonic tricarboxylic acids, namely, the pairs of bilianic and cholanic acids, which these hydroxy-acids yield on oxidation with permanganate. Consequently, cholic acid is a hydroxydeoxycholic acid.

When deoxycholic acid is oxidised by chromic acid, it yields dehydrodeoxycholic acid, $C_{21}H_{29}(CO)_2CO_2H$, and when this is oxidised by alkaline permanganate it gives ψ -cholanic acid, m. p. 259—260° (decomp.). This is another isomeride of cholanic acid, $CO:C_{20}H_{29}(CO_2H)_3$, the constitution of which will be investigated more fully.

J. C. W.

Improved Preparation of Aromatic Aldehydes. GUSTAVE BLANC (*Eng. Pat.*, 115244).—Aromatic aldehydes free from any trace of carboxylic acid are produced by boiling aromatic chloromethylene derivatives with an aqueous solution of an alkali dichromate, preferably with the addition of an alkali hydroxide or carbonate. The reaction is approximately represented by the equation $3R \cdot CH_2Cl + Cr_2O_7 \cdot Na_2 + NaOH = 3NaCl + 3R \cdot CHO + Cr_2O_3 + 2H_2O$. [See, further, *J. Soc. Chem. Ind.*, 1919, June.]

G. F. M.

Terpenes and Ethereal Oils. CXXVI. O. WALLACH (*Annalen*, 1919, **418**, 36—69).—I. *Conversion of Menthone into Pulegone* [with EMMA GROTE].—This work has already been recorded (*A.*, 1918, i, 544).

II. *Eucarvone Series* [with MAX STAUDACHER].—The experiments on the behaviour of halogenated cyclic ketones towards aqueous alkali (*A.*, 1918, i, 440, 442, 444) have been extended to include members of the eucarvone series. β -Dihydroeucarvone (*Annalen*, 1914, **403**, 91), the constitution of which has not yet been ascertained, is smoothly converted by bromine (1 mol.) in cold glacial acetic acid solution into a dibromide, $C_{10}H_{16}OBr_2$, prisms, m. p. 71—72°, which is isomeric with the dibromide, m. p. 68°, obtained by the bromination of tetrahydroeucarvone (*A.*, 1918, i, 444). The new dibromide, m. p. 71—72°, reacts rapidly with warm 2% aqueous potassium hydroxide, yielding volatile products and an acid, $C_{10}H_{16}O_2$. The volatile products have not been obtained in sufficient quantity for complete examination, but they consist chiefly of a ketone which shows no similarity to ketones of the

eucaryone series. It readily forms a *semicarbazone* ($?C_{11}H_{19}O_2N_3$ or $C_9H_{17}ON_3$), crystals, m. p. 194—195°, has an odour of camphor, behaves towards permanganate as an unsaturated compound, and by reduction with hydrogen and palladium yields a saturated ketone (*semicarbazone*, m. p. 196—197°).

The acid, $C_{10}H_{16}O_2$, is shown by direct comparison to be identical with Tiemann and Semmler's α -*cyclogeranic* (*isogeranic*) acid, m. p. 104—105°. Consequently, the dibromide, m. p. 71—72°, probably has the formula $\begin{matrix} \text{CMe}_2\cdot\text{CH}_2\cdot\text{CO} \\ \text{CH}_2\cdot\text{CH}_2\cdot\text{CHBr} \end{matrix} \rightarrow \text{CMeBr}$, and β -dihydroeucaryone has the 7-ring formula originally suggested (*loc. cit.*).

Since the dibromide contains a methylene group adjacent to a carbonyl group, it ought, according to previous experience of the bromination of cyclic ketones (*loc. cit.*), to undergo direct bromination. This is so. By treatment with bromine (1 mol.) in almost boiling glacial acetic acid, it yields a *tribromide*, $C_{10}H_{15}OBr_3$, m. p. 104—105°, which is only slowly attacked by 2% potassium hydroxide at 70°, yielding an *acid*, m. p. about 170°. The isomeric dibromide, m. p. 68°, obtained from tetrahydroeucaryone, does not undergo further bromination under the above conditions. The volatile products obtained when it is shaken with 2% alkali solution (*loc. cit.*) contain a small quantity of a hydrocarbon (?), b. p. 138—140°, and a yellow substance, b. p. 93—95°/8 mm., D^{20}_D 0.988, n^{20}_D 1.4813 (these values are only given provisionally), which does not yield any characteristic derivatives, but is converted by reduction with hydrogen and palladium into a *substance*, b. p. 223—225°, D^{20}_D 0.9690, n^{20}_D 1.4690 (*semicarbazone*, $C_{11}H_{21}ON_3$, m. p. 212—213°; *oxime*, m. p. 55—56°), which is probably a cyclic ketone having its oxygen atom in a side-chain.

The acid, $C_{10}H_{16}O_2$, m. p. 91.5—92.5°, obtained by the action of 2% potassium hydroxide on dibromotetrahydroeucaryone (*loc. cit.*), is converted by oxidation with alkaline permanganate into a mixture of three acids, $C_{10}H_{16}O_3$, m. p. 159—160°, $C_{10}H_{14}O_3$, m. p. 187°, the third acid, m. p. 90—91°, being produced in very small quantity.

Since the preceding brominated 7-ring ketones of the eucaryone series differ from halogenated 6-ring ketones in yielding volatile products as well as an acid by treatment with 2% potassium hydroxide, *dibromosuberone*, $C_7H_{10}OBr_2$, m. p. 70—72°, has been shaken with dilute potassium hydroxide solution at 70°, whereby a volatile ketone (*semicarbazone*, m. p. 190—191°) and an acid, probably tetrahydrobenzoic acid, have been obtained. C. S.

Adsorption of the Glucosides of Digitalis Leaves. C. MANNICH (*Ber. Deut. pharm. Ges.*, 1919, **29**, 206—213).—Experiments with gitalin showed the latter to be readily adsorbed from aqueous solution by blood charcoal (the latter can adsorb at least 20% of its weight), less readily from alcoholic solution, and still less readily from solution in chloroform. A specimen of charcoal containing 20% of gitalin did not lose glucoside when treated with

water, and only a portion when alcohol was used, but practically all of it was removed by chloroform. Other substances, such as fuller's earth, the sulphides of lead, copper, or zinc, and particularly those of arsenic and antimony, have the power of adsorbing the bitter principles from an aqueous extract of digitalis leaves. Attempts to isolate the glucosides by treatment of infusion of digitalis with animal charcoal and subsequent extraction of the latter with chloroform did not lead to the desired result, possibly because the principles are not free in the aqueous solution, but in complex compounds with other substances, such as tannins.

The author considers that the readiness with which the digitalis glucosides are adsorbed by the powdered drug explains the difficulty of their complete extraction, and also the better results which are obtained when water, as solvent, is replaced by alcohol. H. W.

Syntheses of Depsides, Lichen Substances, and Tannins.

II. EMIL FISCHER (*Ber.*, 1919, 52, [B], 809—829).—A general résumé of the progress made by Fischer and his co-workers in this field since the year 1913; the individual subjects have been previously abstracted. H. W.

Tannin and the Synthesis of Similar Substances. VI.

EMIL FISCHER and MAX BERGMANN (*Ber.*, 1919, 52, [B], 829—854, Compare A., 1912, i, 471, 887; 1913, i, 479; 1915, i, 437; 1918, i, 87).—The removal of acetyl groups from substances such as the acetates of galloyl- and digalloyl-glucose, previously effected with cold alkali or with warm sodium acetate solution, can also be effected at the ordinary temperature by a moderate amount of concentrated aqueous hydrochloric acid in methyl-alcoholic solution. If the acetyl derivative is too sparingly soluble in methyl alcohol, a mixture of the latter with acetone may be used. The penta(*m*-digalloyl)- α - and - β -glucoses obtained in this manner from the acetates are optically purer than those previously obtained. The method can also be applied with good results to simpler substances, such as acetylsalicylic acid and triacetylgallic acid.

The use of the potassium salt for the purification of tannins was recommended by Berzelius. The authors find the most convenient method of preparation to consist in mixing alcoholic solutions of the natural or synthetic tannins and potassium acetate, but the precipitates contain small quantities of the latter. The salts from Chinese tannin, pentadigalloyl- α -glucose, pentadigalloyl- β -glucose, and pentagalloyl glucose have $[\alpha]_D +46.3^\circ$, $+56.6^\circ$, and $+33.7^\circ$, respectively, in water. The salt appears to be suitable for the separation of artificial tannins from many other substances and for their purification, but not suitable for the differentiation of the individual galloyl glucoses.

Attempts have been made to extend the method used in the preparation of 1-monogalloyl- β -glucose (this vol., i, 89) to other 1-acylglucoses, but the results are disappointing, as frequently the acyl group is removed simultaneously with the acetyl groups. This

is, for example, the case with *1-benzoyltetra-acetyl- α -glucose*, long, colourless needles, m. p. 60—63°, but frequently several degrees lower, owing possibly to dimorphism, $[\alpha]_D^{25} + 113.5^\circ$ in chloroform. On the other hand, *1-p-acetoxylbenzoyltetra-acetyl- β -glucose*, colourless needles, m. p. 172—173° (corr.), $[\alpha]_D^{25} - 30.6^\circ$ in *s*-tetrachloroethane, could be converted by alcoholic sodium hydroxide or alcoholic ammonia into *1-p-hydroxybenzoyl- β -glucose*, flat needles, m. p. about 228° (corr.; decomp.) when rapidly heated, $[\alpha]_D^{25} - 23.9^\circ$ in *s*-tetrachloroethane; in the latter case, *1-p-hydroxybenzoyltetra-acetyl- β -glucose*, m. p. 196—197° (corr.), $[\alpha]_D^{25} - 38.4^\circ$ in acetone, is formed as intermediate product. Similarly, *1-p-acetoxylbenzoyltetra-acetyl- α -glucose*, m. p. 134—135° (corr.), $[\alpha]_D^{25} + 116^\circ$ in *s*-tetrachloroethane, could be deacetylated with alcoholic sodium hydroxide, but the product was a syrup which could not be caused to crystallise or reconverted into the pure penta-acetate.

The catalytic action of sodium alkoxide on esters in alcoholic solution has been applied for the removal of acetyl groups. Thus, for the elimination of the five acetyl groups of *p*-acetoxylbenzoyltetra-acetylglucose dissolved in alcohol, one molecule of sodium ethoxide is sufficient at the ordinary temperature, and the presence of a small quantity of water in the alcohol does not hinder the reaction; these conditions are particularly advantageous for securing good yields. The method has also been applied to the isolation of dextrose from its penta-acetate and of α -methylglucoside from its tetra-acetate.

Attempts to prepare 1-galloyl- α -glucose are described. It is found that the specific rotation of 1-galloyl- β -glucose gradually changes from negative to positive, and finally attains a maximum when its aqueous solution is agitated with calcium carbonate, or, more rapidly, with sodium carbonate or pyridine; in all probability, the change in sign is caused by the conversion of 1-galloyl- β -glucose into the α -derivative, but attempts to isolate the latter from the product were not successful. Crude tetra-acetyl- α -glucose, obtained by inversion of the β -compound, was therefore treated with triacetylalloyl chloride in the presence of quinoline, whereby ultimately *triacetylalloyltetra-acetyl- α -glucose*, microscopic needles, m. p. 158—159° (corr.), $[\alpha]_D^{25} + 99.9^\circ$ in *s*-tetrachloroethane, was isolated; this was then hydrolysed with alcoholic ammonia, but the product was not crystalline. It appeared, however, to contain considerable amounts of 1-galloyl- α -glucose, since, on re-acetylation, it yielded the hepta-acetyl derivative in quantity.

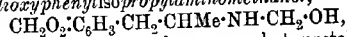
The galloyl derivatives of the sugars differ among themselves in their behaviour towards gelatin solutions. The penta- and tri-galloyl compounds precipitate the latter from aqueous solution in the same manner as do the tannins, but this property is not shown by the varying monogalloyl glucoses nor by monogalloyl fructose. Since similar differences were to be expected among the polyhydroxy-alcohols, the derivatives of glycol, trimethyleneglycol, glycerol, erythritol, and mannitol have been prepared and ex-

aminated. They are readily obtained from the alcohols by coupling with triacetylalloyl chloride and subsequent removal of the acetyl groups. The crystalline *ethyleneglycol digallate* is so sparingly soluble in water or alcohol that its reaction with gelatin and arsenic acid cannot be investigated. With *trimethyleneglycol digallate*, the gelatin test is not characteristic, but distinct gelatinisation is caused by arsenic acid in alcoholic solution. *Erythritol tetragallate* is readily soluble in water and coagulates gelatin, but the alcoholic solution is too dilute to be tested with arsenic acid. The amorphous *glyceryl trigallate* and *mannitol hexagallate* yield colloidal solutions in water and behave like tannins towards both reagents. The physical properties of this series of substances are as follows: *ethyleneglycol ditriacetyl-gallate*, colourless leaflets, m. p. $172-173^{\circ}$ (corr.) after slight softening; *ethyleneglycol digallate*, microscopic needles, which decompose at about 287° (corr.) without melting; *glyceryl tri-triacetyl-gallate*, amorphous powder; *glyceryl trigallate*, pale yellow, amorphous, brittle mass. [With (FRL.) HERTHA VON PELCHERZIM.]—*Trimethyleneglycol ditriacetyl-gallate*, leaflets, m. p. $159-160^{\circ}$; *trimethyleneglycol digallate*, leaflets, m. p. about 270° (decomp.); *erythritol tetra-triacetyl-gallate*, small, colourless needles without definite m. p.; *erythritol tetragallate*, which when rapidly heated darkens at about 288° , and is completely decomposed at about 308° ; *mannitol hexa-triacetyl-gallate*, amorphous, pale brown substance; *mannitol hexa-gallate*, amorphous, pale brown substance, $[\alpha]_D^{25} + 27.0^{\circ}$ in alcohol. H. W.

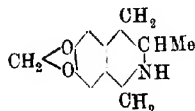
The Resolution of Hyoscine and its Components, Tropic Acid and Oscine. HAROLD KING (T., 1919, 115, 476—508).

A New Synthesis of Hydrastinine and its Homologues. KARL W. ROSENMUND (Ber. Deut. pharm. Ges., 1919, 29, 200—206).—Starting from methylenedioxyphenylisopropylamine, the synthesis of certain homologues of hydrastinine has been effected, whilst the alkaloid itself has been prepared from homopiperonylamine by a new method.

Methylenedioxyphenylisopropylaminomethanol,



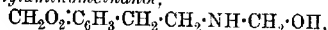
is obtained as a viscous, colourless, somewhat unstable oil by the action of chloromethyl alcohol on methylenedioxyphenylisopropylamine in dry ethereal solution, and is converted by warming with 10% aqueous hydrochloric acid into 3-methyldihydronorhydrastinine hydrochloride, m. p. $231-232^{\circ}$; the free base (annexed formula) crystallises in colourless leaflets, m. p. $57-58^{\circ}$; the hydriodide forms colourless leaflets, m. p. $215-217^{\circ}$. Methylation of the base, preferably with formaldehyde, gives 3-methyldihydrohydrastinine, m. p. $85-87^{\circ}$ (hydrochloride, m. p. $230-232^{\circ}$; hydriodide, m. p. 240° ; perchlorate, colour-



less needles, m. p. 215°), which can also be prepared from methylenedioxyphenylisopropylmethylamine. Oxidation with potassium dichromate and sulphuric acid or with iodine leads to the formation of 3-methylhydrastinine, m. p. 107—108° (*hydriodide*, yellow leaflets, m. p. 210—212°; *perchlorate*, greenish-yellow needles, m. p. 212°).

Phenylacetylmethylenedioxyphenylisopropylamine, colourless needles, m. p. 105—106°, is prepared by the action of phenylacetyl chloride on the amine, and is converted by treatment with phosphoric oxide into 1-benzyl-3-methylnorhydrastinine, yellow syrup (*picrate*, m. p. 182°; *hydriodide*, shining prisms, m. p. 208°).

Homopiperonylaminomethanol,



is obtained as a colourless, very unstable oil by the action of chloromethyl alcohol (1 mol.) on homopiperonylamine (2 mols.) in ethereal solution, and is converted by 10% aqueous hydrochloric acid into dihydronorhydrastinine, identical with the product described by Decker (A., 1911, i, 906).

H. W.

Porphyroxine. JITENDRA NATH RAKSHIT (T., 1919, 115, 455—461).

Syntheses in the Indole Series. Homologues of Dinindole and Isatin. J. MARTINET (*Ann. Chim.*, 1919, [ix], 11, 15—84, 85—130).—For the most part a more detailed account of work already published (compare A., 1913, i, 756; 1918, i, 306, 345, 351). The following new compounds are described.

Methyl diacetyl-5-methyldioxindole-3-carboxylate, m. p. 132°, and the corresponding *ethyl ester*, m. p. 110°.

Methyl 5:7-dimethyldioxindole-3-carboxylate, m. p. 260°, and its *diacetyl derivative*, m. p. 227°; the corresponding *ethyl ester*, m. p. 215°, and its *diacetyl derivative*, m. p. 203—204°; *5:7-dimethyldioxindole*, m. p. 228—229°, and its *O-acetyl derivative*, m. p. 201—202°.

Methyl acetyl-1-methyldioxindole-3-carboxylate, m. p. 146°, and the *ethyl ester*, m. p. 65°.

Ethyl 5-bromo-1-methyldioxindole-3-carboxylate, m. p. 160°, and its *acetyl derivative*, m. p. 132°; *5-bromo-1-methyldioxindole*, m. p. 162°, and its *O-acetyl derivative*, m. p. 115°; *5-bromo-1-methylisatinphenylhydrazone*, m. p. 164°.

Ethyl acetyl-1-ethyldioxindole-3-carboxylate, m. p. 68°.

Ethyl 5-bromo-1-ethyldioxindole-3-carboxylate, m. p. 106°, and its *acetyl derivative*, m. p. 120°; *5-bromo-1-ethylisatin*, m. p. 144°, and its *phenylhydrazone*, m. p. 124°.

Methyl 3-hydroxy-2-keto-1-ethyldihydro-ββ-naphthindole-3-carboxylate, m. p. 203°, and its *acetyl derivative*, m. p. 140°, and the *acetyl derivative*, m. p. 114°, of the corresponding *ethyl ester*.

Ethyl 3-acetyl-1:7-trimethylenedioxyindole-3-carboxylate, m. p. 150.

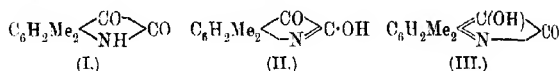
5-Methyl-1:7-trimethylenedioxindole, m. p. 193°; 5-methylisatinphenylhydrazine, m. p. 268°; 1-ethylisatinphenylhydrazine, m. p. 74°; N-ethyl-β-naphthisatinphenylhydrazine, m. p. 180°.

β-Naphthisatoic acid (β-amino-α-naphthylglyoxylic acid) is very unstable, but gives potassium, copper, lead, and silver salts.

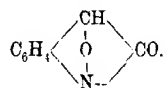
5-Bromo-N-methylisatoic acid (5-bromo-2-methylaminophenylglyoxylic acid) is very unstable, but gives potassium, copper, silver, and lead salts; 5-bromo-N-ethylisatoic acid also gives potassium, copper, silver, and lead salts.

N-Ethyl-β-naphthisatoic acid (β-ethylamino-α-naphthylglyoxylic acid) gives potassium, copper, and lead salts. W. G.

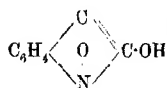
New Isomerides in the Isatin Series. III. GUSTAV HELLER (Ber., 1919, 52, [B]. 437—446. Compare A., 1917, i, 219; 1918, i, 235; this vol., i, 36).—The constitutions of three of the four modifications of 5:7-dimethylisatin have already been established, and the following formulae assigned to them:



In the case of isatin itself, only the isomerides corresponding with these three formulae have been established so far, but it is now found that when the methyl ether of the lactim form (II) of isatin is heated with benzene at 200—205°, it is partly converted into the N-methyl ether of the lactam form (I) and partly demethylated and transformed into a new isomeride which corresponds with the fourth modification of dimethylisatin. This is a feeble base the salts of which are hydrolysed by water. It does not react with diazomethane, methyl iodide, sodium hydrogen sulphite, or Fehling's solution, neither does it form an acetyl or benzoyl derivative nor give the indophenine reaction. It is more soluble in benzene than the other product, and its properties are best expressed in the annexed formula. The compound is designated *isatinone*, and it crystallises in well-developed, dark honey-coloured, quadratic prisms, m. p. 226° (decomp.). It dissolves slowly in 0.5*N*-sodium hydroxide, and if the solution is quickly precipitated by



50% acetic acid, a fifth isomeride, *isatinol* (annexed formula), is obtained in orange-yellow flocks, m. p. 255°, which reverts to



isatinone on crystallisation from glacial acetic acid or benzene. The methyl ether of the fourth modification of dimethylisatin should conform to the same type. If the red solution in sodium hydroxide is exposed to light, however, it becomes pale in time and deposits

Friedländer and Roschdestwensky's anhydro-α-isatinanthranilide.

$$\text{C}_6\text{H}_4 \begin{array}{c} \text{C} \\ \diagup \quad \diagdown \\ \text{C}=\text{N} \\ \diagup \quad \diagdown \\ \text{C} \end{array} \text{C}_6\text{H}_4 \text{ (A., 1916, i, 80).}$$

If the methyl ether of the lactim form of isatin is heated with methyl alcohol at 200° instead of with benzene, it yields this anhydro- α -isatinanthranilide and a hydrate of it, $C_{15}H_{10}O_3N_2$, colourless crystals, m. p. 172°, which yields anthranoylanthranilic acid when boiled with alcoholic potassium hydroxide.

J. C. W.

An Improved Method of Preparing Indican from Indigo-yielding Plants. BHAILAL M. AMIN (*Agric. Res. Inst. Pusa, Indigo Publ. No. 5*).—The method, which is far more rapid than any of the methods hitherto described, consists in extracting the fresh leaf with hot water so as to dissolve the indican. Freshly slaked lime is added to the extract to precipitate impurities, such as amino-acids, tannins, gums, etc. The purified liquor is filtered, evaporated, and the indican extracted from the concentrated solution with acetone. The wet extract is evaporated to remove the acetone, and on cooling in ice the aqueous solution which is left, indican hydrate separates. The crude hydrate is purified by dissolving it in absolute alcohol and precipitating with benzene, when pure anhydrous indican crystallises. This method gives an excellent yield (70–80%), and can be applied to any species of plant, and by its use pure indican has, for the first time, been prepared in large quantities from Java indigo (*Indigofera arrecta*).

W. G.

New Transitions from the Indole to the Quinoline Series.

GUSTAV HELLER (*Ber.*, 1919, **52**, [B], 741–745).—It has been previously shown (Heller and Wunderlich, *A.*, 1914, i, 865) that 2-cyano-2:3-dihydroindole-2-carboxylamide is converted by nitrous fumes into 2-hydroxyquinoline-3-carboxylamide. A similar conversion of the 5-membered to the 6-membered ring occurs when diazomethane acts on an ethereal suspension of isatin, 2:3-dihydroxyquinoline, needles, m. p. 190–192°, being obtained (compare Madelung, *A.*, 1913, i, 91). The latter, with more diazomethane, appears to yield a monomethyl ether; with acetic anhydride, it gives a monoacetyl derivative, long needles, m. p. 214–215°.

Under similar conditions, *dihydroxy-6:8-dimethylquinoline*, m. p. about 242° (decomp.), is obtained from 2:4-dimethylisatin lactam, whilst 2:4-dimethylisatin lactim yields a *product*, aggregates of needles, m. p. 253° (decomp.).

Dimethylisatol and dimethylisatinone are normally alkylated by diazomethane, yielding, however, different substances, which are insoluble in alkali. Oxindole, dioxindole, and phthalimidine are not attacked by ethereal solutions of diazomethane.

H. W.

Action of Organomagnesium Compounds on Quinoline Methiodide. Stereochemistry of Compounds of Nitrogen.

MARTIN FREUND and ELISABETH KESSLER (*J. pr. Chem.*, 1918, [ii], **98**, 233–254. Compare *A.*, 1905, i, 156; 1909, i, 417).—The action of magnesium propyl bromide on quinoline

methiodide yields 1-methyl-2-propyldihydroquinoline, $C_{13}H_{17}N$, as a golden-yellow, unstable oil, b. p. 268—270° (compare von Braun and Aust, A., 1915, i, 586); the *picrate* forms needles, m. p. 157—158°. The base combines with methyl iodide, yielding a crystalline *methiodide*, m. p. 158—160° (decomp.), which is converted at its melting point or by crystallisation from dilute alcohol into a compound, $C_{13}H_{16}NI$, m. p. 184°, which is identified as 2-propylquinoline methiodide. 1 : 2-Dimethyl-1 : 2-dihydroquinoline *methiodide*, yellowish-red crystals, m. p. 212—213°, does not exhibit similar behaviour. The dihydro-base does not yield crystalline salts; it combines with bromine, yielding a *perbromide*, $C_{13}H_{17}NBr_4$, needles, m. p. 158°, which, when treated with sulphurous acid and subsequently with sodium iodide, 'gives 3(4)-bromo-1-methyl-2-propyl-1 : 2-dihydroquinoline *hydriodide*, a yellow, crystalline salt, m. p. 242°, after darkening at 235°. The base is reduced by tin and hydrochloric acid to 1-methyl-2-propyltetrahydroquinoline, b. p. 270—280° (compare von Braun and Aust, *loc. cit.*), which, when obtained in this manner, appears to be a mixture of two bases, one of which has b. p. 274—278° and forms a crystalline *hydrochloride*, long needles, m. p. 237—238°, *hydrobromide*, needles, m. p. 223—224°, and *hydriodide*, m. p. 176° after softening at 168°, but does not give a crystalline methiodide, whilst the other, b. p. 272—276°, does not yield crystalline salts, but forms a crystalline *methiodide*, colourless leaflets, m. p. 196—197° after some decomposition at 190°.

The action of magnesium *isobutyl* iodide on quinoline methiodide has been similarly studied with the object of discovering further instances of stereoisomerism of similar character. 1-Methyl-2-*isobutyl*dihydroquinoline forms an unstable oil, b. p. 278—280° (*picrate*, shining needles, m. p. 154—155°; the *methiodide* is not crystalline), which, as in the case of the propyl compound, is reduced to a mixture of bases, b. p. 260—280°, separable by means of their hydrochlorides. The one of these is a pale yellow, almost odourless oil, b. p. 283° (*hydrochloride*, transparent needles, m. p. 223—224°; *hydrobromide*, m. p. 225° after previous softening; *hydriodide*, m. p. 183—184°; *methiodide*, m. p. 168°), whilst the other is darker in colour, less pleasant in odour, has b. p. 263°. forms readily soluble salts with the halogen acids, and gives a *methiodide*, m. p. 174° after previous softening.

1-Methyl-2-*isopropyl*dihydroquinoline is a yellow, unstable oil, b. p. 268—274° (*picrate*, needles, m. p. 184°); it is reduced by tin and hydrochloric acid to 1-methyl-2-*isopropyl*tetrahydroquinoline, b. p. 265—266°. In this instance, the separation of possible isomerides could not be effected by means of halogen acids, owing to the solubility of the salts formed. Probably a mixture of stereoisomerides is present, since the crystalline *methiodide* (yellow needles, m. p. 179—180°) isolated from the crude base does not correspond in quantity with the weight of base used.

2-Benzyl-1-methyldihydroquinoline is obtained in poor yield by

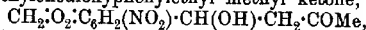
the action of magnesium benzyl chloride on quinoline methiodide; the crude product is separable into two fractions, b. p. 125–140°/13–20 mm. and 140–155°/13–20 mm. respectively.

3-Bromo-2-phenyl-1-methyldihydroquinoline, b. p. 270°/75 mm., forms a brown, feebly basic oil, which has only a slight tendency towards salt formation; the *picrate* crystallises in four-sided leaflets, m. p. 185° after softening at 175°.

H. W.

Some Derivatives of 6:7-Dihydroxyquinoline. W. BORSCHÉ and R. QUAST (*Ber.*, 1919, **52**, [B], 432–437).—A good method for the preparation of Haber's 6:7-methylenedioxy-2-methylquinoline is described (compare A., 1891, 705).

Piperonaldehyde is nitrated, and the 6-nitro-derivative, which is formed in good yield, is condensed with acetone in the presence of 3% potassium carbonate, whereby a 75% yield of β -hydroxy- β -6-nitro-3:4-methylenedioxyphenylethyl methyl ketone,



is obtained (compare Herz, A., 1905, i, 778). This is reduced by means of zinc dust in a mixture of acetic and hydrochloric acids, an excellent yield of 6:7-methylenedioxy-2-methylquinoline being obtained. The base has m. p. 150°, b. p. 306–308°/743 mm., and forms a *methiodide*, m. p. 277–278°, and a *methochloride*, m. p. 265–266°, which gives a *double salt* with mercuric chloride, m. p. 193° (decomp.). It condenses with benzaldehyde under the influence of zinc chloride to form 2-styryl-6:7-methylenedioxyquinoline, m. p. 179–180°, and it suffers reduction by sodium and alcohol to 6:7-methylenedioxy-2-methyl-1:2:3:4-tetrahydroquinoline, $\text{CH}_2:\text{O}_2:\text{C}_6\text{H}_2<\begin{smallmatrix} \text{CH}_2\cdot\text{CH}_2 \\ \text{NH}\cdot\text{CHMe} \end{smallmatrix}$. This is a snow-white base,

m. p. 44–45°, which forms a *nitroso*-compound, yellow needles, m. p. 85–86°, and a *methiodide*, m. p. 176–177°.

The corresponding phenylquinoline has also been prepared. Piperonylideneacetophenone is nitrated, and the *phenyl 2-nitro-4:5-methylenedioxy-styryl ketone* so formed, which crystallises in flat, yellow needles, m. p. 165–166°, is reduced by zinc dust and a mixture of acetic and hydrochloric acids. 6:7-Methylenedioxy-2-phenylquinoline, $\text{CH}_2:\text{O}_2:\text{C}_6\text{H}_2<\begin{smallmatrix} \text{CH}\cdot\text{CH} \\ \text{N}=\text{CPh} \end{smallmatrix}$, crystallises in very pale yellow leaflets, m. p. 110°, and its *picrate* has m. p. 192°.

J. C. W.

ψ -1:8-*iso*Naphthoxazones. BIMAN BIHARI DEY and MAHENDRA NATH GOSWAMI (*T.*, 1919, **115**, 531–541).

The Asymmetric Nitrogen Atom. LI. Abnormal Quaternary Ammonium Salts. E. WEDEKIND and TH. GOOST (*Ber.*, 1919, **52**, [B], 446–459).—In the last communication (A., 1916, i, 671), a diquaternary ammonium salt was described having two asymmetric nitrogen atoms of unlike asymmetry, namely, the

n^o

salt of the formula $\text{NMePh}(\text{C}_7\text{H}_7)\text{Br}\cdot\text{C}_3\text{H}_6\cdot\text{NMePh}(\text{C}_3\text{H}_5)\text{I}$. With the hope of obtaining similar salts, experiments have been conducted with *pp'*-dimethyldiethyldiaminodiphenylmethane. When this is treated with one molecular proportion of benzyl bromide or allyl iodide, normal addition takes place (Fröhlich, A., 1911, i, 493), but *sec*-butyl iodide does not react, and propyl bromide or iodide, and *isobutyl* and ethyl iodides give abnormal products of the type $2[\text{CH}_2(\text{C}_6\text{H}_4\cdot\text{NMeEt})_2]\cdot\text{RX}$.

The abnormal propiodide has been studied most completely. Attempts to convert it into the corresponding chloride, bromide, nitrate, or camphorsulphonate give rise to the free ditertiary base and the normal amino-ammonium salt, which can be precipitated as the normal iodide on the addition of potassium iodide. Silver oxide gives the same result. By treatment with silver perchlorate, however, an abnormal perchlorate may be obtained. The salt is also decomposed into the base and normal iodide by the action of aqueous-alcoholic ammonia, and benzyl bromide reacts in a manner which is to be interpreted in the same way.

The normal iodide combines with the base to form the abnormal salt, and reacts with benzyl bromide to form a salt with two unlike asymmetric nitrogen atoms of the desired type. Attempts to resolve this into the expected four optical isomerides gave no definite results.

The "*abnormal propiodide*," $(\text{C}_{19}\text{H}_{26}\text{N}_2)_2\cdot\text{C}_3\text{H}_7\cdot\text{I}$, is best obtained by heating equimolecular proportions of the base (Fröhlich, *ibid.*) and propyl iodide at 100° in a sealed tube. It crystallises from methyl alcohol with m. p. 153° , and its solutions become deep blue on exposure to the air. The abnormal perchlorate has m. p. $133\cdot5^\circ$. The normal iodide, *methylethylpropyl-methylethylamino-diphenylmethane-ammonium iodide*,

$\text{NMeEt}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMeEtPrI}$, has m. p. $158\cdot5^\circ$, the corresponding nitrate has m. p. $155\cdot5^\circ$, and the first crystals of the *d*-camphorsulphonate have $[\text{M}]_D + 59\cdot72^\circ$, which is about the same as that of the anion itself.

Diphenylmethanediammonium-(methylethylpropyl iodide)-(methylethylbenzyl bromide),

$\text{NMeEt}(\text{C}_7\text{H}_7)\text{Br}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMeEtPrI}$, obtained by the action of benzyl bromide on the normal iodide, is separated by alcohol into a sparingly soluble fraction, decomposed about 175° , and a semi-solid portion. The *di-iodide* corresponding with the first fraction has m. p. 187° , and the *diperchlorate*, m. p. 225° , whilst the salts of the second portion have m. p.'s 182° and 222° respectively. The mixture of diperchlorates has m. p. 221° , and can be isolated from the product of the action of benzyl bromide on the abnormal iodide.

The base also forms an "*abnormal ethiodide*," m. p. $144\text{--}145^\circ$, and "*abnormal isobutiodide*," m. p. $140\text{--}141^\circ$, but methyl iodide converts it into *diphenylmethane-pp'-bisdimethylethylammonium di-iodide*, $\text{CH}_2(\text{C}_6\text{H}_4\cdot\text{NMe}_2\text{EtI})_2$, colourless needles, m. p. 203° .

J. C. W.

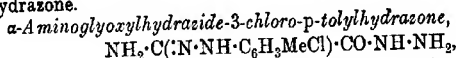
I. Syntheses and Reactions of New Monoaryl-hydrazidine Carboxylic Esters. II. Oxidative Fission by means of Chlorine of Organic Substances containing the Hydrazone and Hydrazidrazone Groups. (I.) CARL BÜLOW and RICH. ENGLER. (II.) CARL BÜLOW (*Ber.*, 1919, **52**, [B], 632—651).—In continuation of the work of Bülow and Engler (this vol., i, 47), the authors have now prepared ethyl α -aminoglyoxylate 3-chloro-*p*-tolylhydrazone, the corresponding amide and hydrazide, and have made an extended study of their reactions. They are led to the following general conclusions: Benzaldehyde arylhydrazones and their derivatives are primarily converted into pure chlorinated products by treatment with chlorine in a suitable solvent; as secondary change, the hydrazone is converted into the corresponding diazonium or chloroaryldiazonium group. The arylhydrazone residue is eliminated from hydrazidines or amidrazones as diazonium salt by the agency of chlorine. Nitrogen is eliminated by chlorine from acid hydrazidrazones and azines, but the fate of the remainder of the molecule has not yet been elucidated.

Ethyl α -aminoglyoxylate-3-chloro-*p*-tolylhydrazone is obtained as colourless, shining leaflets, m. p. 86° , by the action of alcoholic ammonia at the ordinary temperature on ethyl α -chloroglyoxylate-3-chloro-*p*-tolylhydrazone. The hydrochloride has m. p. 173 — 174° . The ester is readily decomposed by chlorine in acetic acid solution, and the diazonium salt of 3-chloro-*p*-toluidine which is produced is readily identified by coupling it with β -naphthol, the product forming long, red needles, m. p. 179 — 179.5° . Boiling concentrated aqueous hydrochloric acid decomposes the ester, yielding ammonium chloride, oxalic acid, and 3-chloro-*p*-tolylhydrazine hydrochloride; on account of its instability, the free base was not investigated. It reacts with *m*-nitrobenzaldehyde to yield *m*-nitrobenzaldehyde-3-chloro-*p*-tolylhydrazone, m. p. 175° , which is decomposed by nitric acid with production of a diazonium salt; this, with chlorine in acetic acid solution, gives the substance, $C_{11}H_{10}O_2N_3Cl$, long, yellow needles, m. p. 139° . 2:5-Dichlorobenzaldehyde-3-chloro-*p*-tolylhydrazone, slender needles, has m. p. 108° , and also yields a diazonium salt when treated with concentrated nitric acid, and a substance, m. p. 114 — 115° , when acted on by chlorine. The constitution of the hydrazine is definitely decided by preparation of the condensation products with *m*-nitrobenzaldehyde and 2:5-dichlorobenzaldehyde from synthetic 3-chloro-*p*-tolylhydrazine, and the identity of the products thus obtained with those previously prepared.

α -Aminoglyoxylamide-3-chloro-*p*-tolylhydrazone.

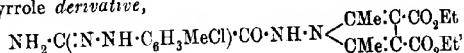
$NH_2C(N \cdot NH \cdot C_6H_3MeCl) \cdot CO \cdot NH_2$, thick, grayish-white needles, m. p. 170 — 171° , is prepared by the more protracted action of alcoholic ammonia on ethyl α -chloroglyoxylate 3-chloro-*p*-tolylhydrazone; it is completely decomposed by nitric acid, and is quantitatively decomposed by chlorine, yielding a diazonium salt and a substance, $C_9H_{11}ON_4Cl$. The hydrazone

may also be prepared from α -chloroglyoxylamide-3-chloro-*p*-tolylhydrazone.



colourless prisms, m. p. 199° , prepared by the action of hydrazine hydrate on the corresponding ester, is immediately decomposed by nitric acid, and undergoes oxidative fission by chlorine in a complicated manner, yielding large amounts of diazo-compound. The hydrazide readily yields compounds with benzaldehyde (yellow, rhombic leaflets, m. p. 203°), *p*-hydroxybenzaldehyde (pale yellow needles, m. p. 245°), *m*-hydroxybenzaldehyde (crystalline powder, m. p. 234°), 2:5-dichlorobenzaldehyde (yellow prisms, m. p. 262°), vanillin (small, colourless needles, m. p. 215°), and, less readily, with acetophenone (long needles, m. p. 229°). In each case, fission by chlorine occurs in two stages: (1) evolution of nitrogen, and (2) formation of diazonium salt. The compound with acetophenone is further remarkable for the ease with which it is decomposed into its constituents by concentrated hydrochloric acid.

The hydrazide reacts also with ethyl diacetylsuccinate to yield the pyrrole derivative,

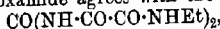


almost colourless rhombohedra, m. p. 228° . The compound is decomposed by nitric acid, yielding a diazonium salt, and also by chlorine; in the latter case, nitrogen is not evolved, the products being a diazonium salt and a residue containing the pyrrole nucleus.

H. W.

Diketopiperazines. VII. Action of Oxalyl Chloride on Alkylloxamides. J. V. DUBSKY and F. BLUMER (*Ber.*, 1919, 52, [B], 215—217. Compare A., 1916, i, 635, 636, 672; 1918, i, 138, 189).—When alkylloxamides are heated with oxalyl chloride under reflux, they yield tetraketo-1-alkylpiperazines. Thus, methyl-oxamide forms the known methyl derivative, $\text{NMe} \begin{matrix} \text{CO}\cdot\text{CO} \\ \text{CO}\cdot\text{CO} \end{matrix} \text{NH}$,

which confirms the constitution of this compound (*ibid.*, 635), whilst tetraketo-1-ethylpiperazine crystallises in small leaflets, m. p. 235° . Using benzene as a diluent, however, the compound obtained from ethylloxamide agrees with the formula

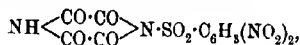


and has m. p. 175° (clear at 187°). Oxamide itself does not undergo such reactions.

J. C. W.

Diketopiperazines. VIII. Action of Absolute Nitric Acid on 3:5-Diketo-1-benzenesulphonylpiperazine. J. V. DUBSKY and F. BLUMER (*Ber.*, 1919, 52, [B], 218—220).—3:5-Diketo-1-benzenesulphonylpiperazine is very stable toward

pure nitric acid, with which it only reacts on boiling, the product being a compound, probably of the formula



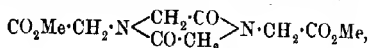
which forms a frothy mass at 124°, becoming clear at 130°.

The piperazine derivative was obtained by Johnson's method (A., 1906, i, 157) after the following alternative process was found to be fruitless. Methyl iminodiacetate is converted into its benzenesulphonyl derivative, needles, m. p. 55–57°, and then into benzenesulphoniminodiacetamide, $\text{SO}_2\text{Ph} \cdot \text{N}(\text{CH}_2\text{CO} \cdot \text{NH}_2)_2$, needles, m. p. 164°, which only loses a little ammonia when kept molten for an hour, and yields scarcely any sublimate when heated at 350°/10 mm.

J. C. W.

Diketopiperazines. IX. Action of Absolute Nitric Acid

on 3:5-Diketo-1-ethylpiperazine. J. V. DUBSKY and F. BLUMER (Ber., 1919, 52, [B], 221–225).—When methyl iminodiacetate is distilled, the residue apparently contains a condensation product, namely, methyl 2:5-diketopiperazine-1:4-diacetate,



m. p. 96–97°. The purified distillate (A., 1918, i, 188) is ethylated by means of ethyl sulphate, and the methyl ethyliminodiacetate, b. p. 111–113°/8 mm., is converted into ethyliminodiacetamide, $\text{NEt}(\text{CH}_2\text{CO} \cdot \text{NH}_2)_2$, by means of alcoholic ammonia. This has m. p. 137–140°, forms a hydrochloride, m. p. 206–208°, and a nitrate, m. p. 172°, and when heated at 250°/10 mm. gives a sublimate of 3:5-diketo-1-ethylpiperazine, $\text{NEt} \begin{array}{c} \diagup \text{CH}_2 \cdot \text{CO} \diagdown \\ \diagdown \text{CH}_2 \cdot \text{CO} \diagup \end{array} \text{NH}$, m. p. 74°. This yields a hydrochloride, small leaflets, and a nitrate, m. p. 145–148°, which dissolves in pure nitric acid to form a compound, $\text{C}_4\text{H}_5\text{O}_3\text{N}$, decomp. about 98°. J. C. W.

Diketopiperazines. X. J. V. DUBSKY [with ST. IZDEBSKA-DOMANSKA, M. SPRITZMANN, W. D. VAN LIER-WENSINK, and CH. GRÄNACHER] (Ber., 1919, 52, [B], 225–234).—An account of the preparation of some diketopiperazines and their behaviour towards nitric acid.

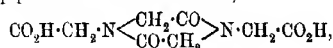
3:5-Diketo-1-phenylpiperazine.—This compound has been made in three ways: (a) by heating equal quantities of aniline and chloroacetamide at 120°, whereby the temperature suddenly rises to 210°, and then sinks again (Bischoff, A., 1889, i, 1015); (b) by heating phenyliminodiacetamide in a vacuum-sublimation apparatus (Bischoff, A., 1898, i, 10); (c) the best way, by heating together chloroacetamide and anilinoacetamide at 100–170°, the latter compound being prepared by heating aniline, chloroacetamide, and fused sodium acetate at 120–140°. When dissolved in ice-cold, absolute nitric acid, the piperazine forms a

yellow *dinitro*-derivative, $C_6H_5(NO_2)_2 \cdot N < \begin{smallmatrix} CH_2 \cdot CO \\ CH_2 \cdot CO \end{smallmatrix} > NH$, decomp. 105° .

3:5-Diketo-1:4-diphenylpiperazine.—Aniline and phenylimino-diacetic acid are condensed to the mono-anilide (Hausdörfer, A., 1889, 1013), and this is heated with benzene and acetic anhydride at 150 – 160° . The 3:5-diketo-1:4-diphenylpiperazine (*ibid.*) yields a mixture of di- and tri-nitro-derivatives with pure nitric acid.

3:5-Diketo-1-p-tolylpiperazine, glistening scales, m. p. 190 – 192° , from *p*-toluidine and chloroacetamide, forms a yellow *dinitro*-compound, m. p. about 110° (decomp.).

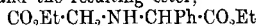
2:5-Diketopiperazine-1:4-diacetic acid,



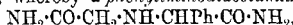
decomp. 280 – 290° , is not affected by solution in pure nitric acid.

2:5-Diketo-1-phenylpiperazine, pearly leaflets, m. p. 245° , obtained by the action of ammonia on chloroacetylphenylglycine (Leuchs and Manasse, A., 1907, i, 770), yields a sulphur-yellow *nitro*-compound, $NO_2 \cdot C_6H_4 \cdot N < \begin{smallmatrix} CO \cdot CH_2 \\ CH_2 \cdot CO \end{smallmatrix} > NH$, m. p. 247 – 252° .

Some attempts to prepare 3:5-diketo-2-phenylpiperazine are described. In the most successful scheme, glycine ester hydrochloride, benzaldehyde, potassium cyanide, ether, and water were shaken together, and the resulting ester,



(Stadnikoff, A., 1909, i, 106), was left with methyl-alcoholic ammonia at 0° , whereby *α*-phenyliminodiacetamide.



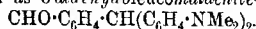
m. p. 152 – 153° , was formed. This did not, however, yield the expected piperazine on sublimation. J. C. W.

Mercury Mercaptide Nitrites and their Reaction with the Alkyl Iodides. V. Chain Compounds of Sulphur (*continued*).

SIR PRAFULLA CHANDRA RAY and PRAFULLA CHANDRA GUHA (T., 1919, 115, 541–548).

Condensation Products of *o*-Phthalaldehyde. IV. Condensation of *o*-Phthalaldehyde with Dimethylaniline. ERNST WEITZ (*Annalen*, 1919, 418, 1–28. Compare Thiele and Weitz, A., 1910, i, 854).—This condensation follows very different courses according to the experimental conditions. When *o*-phthalaldehyde, dimethylaniline (more than 6 mols.), and anhydrous zinc chloride are heated together at 120 – 130° for two hours, the chief product is a *substance*, $C_{40}H_{46}N_4$, almost colourless, crystalline powder, m. p. 245° , which can only be the *leuco-base* of *o*-phthalaldehyde-green, $C_8H_4(CH[C_6H_4 \cdot NMe_2])_2$. When *o*-phthalaldehyde, dimethylaniline (2 mols.), and anhydrous zinc chloride are heated together at 100 – 110° for one hour, the chief product is a *substance*, $C_{24}H_{26}ON_2$, crystals, brownish-red when massive, almost

colourless when powdered or in solution, m. p. 143—144°, which is converted into the preceding leuco-base by further heating with dimethylaniline and zinc chloride, reacts additively with acetic anhydride (1 mol.) in the presence of a few drops of sulphuric acid to form the *diacetate*, $C_{28}H_{32}O_4N_2$, m. p. 117—118°, and is therefore regarded as *o*-aldehydoleucomalachite-green,



By oxidation, both *leuco*-bases yield dyes which are almost olive-green.

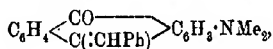
When *o*-phthalaldehyde and dimethylaniline are condensed by heating with concentrated hydrochloric acid on the water-bath, the product is a *substance*, $C_{24}H_{19}O_2N$, garnet-red leaflets, m. p. 163°, which behaves as a weak base (*picrate*, brown crystals, m. p. 170°, decomp. from about 150°). The substance reacts additively with 1 mol. of acetic anhydride (and sulphuric acid), forming a *diacetate*, $C_{28}H_{25}O_4N$, red prisms, m. p. 172°, yields a *nitro*-derivative, $C_{24}H_{18}O_4N_2$, red crystals, m. p. 183°, by treatment with aqueous sodium nitrite in 25% sulphuric acid solution, absorbs 1 mol. of hydrogen in acetone or 70% alcoholic solution by treatment by the Paal-Skita method, and 1 mol. of bromine in glacial acetic acid solution (in neither case could a well-defined additive product be isolated), and yields benzil-2:2'-dicarboxylic acid by oxidation with boiling alkaline permanganate solution. By oxidation in alcoholic solution at the ordinary temperature with 6% hydrogen peroxide solution and 2*N*-sodium hydroxide, the base yields 2-*p*-dimethylaminobenzoylbenzoic acid, *p*-dimethylamino-phenylphthalide, and a *lactone*, $C_{24}H_{19}O_3N$, yellow crystals, m. p. 163°.

On the evidence of the preceding reactions, the red base, $C_{24}H_{19}O_2N$, might be dimethylamino-*o*-aldehydobenzylidene-anthrone, $CHO \cdot C_6H_4 \cdot CH : C \begin{matrix} \swarrow C_6H_4 \\ \searrow C_6H_3(NMe_2) \end{matrix} > CO$, or 2-*o*-aldehydo-

phenyl-3-*p*-dimethylaminophenylindone, $CHO \cdot C_6H_4 - \begin{matrix} \text{C} \cdot \text{CO} \\ | \\ NMe_2 \cdot C_6H_4 \cdot \text{C} \cdot C_6H_4 \end{matrix}$. Since, however, 10-benzylideneanthrone and 2-dimethylamino-10-benzylideneanthrone (following abstract) respectively yield anthraquinone and 2-dimethylaminoanthraquinone by oxidation, whilst 2:3-diphenylindone yields phenylphthalide and *o*-benzoylbenzoic acid, there can be little doubt that the red base, $C_{24}H_{19}O_2N$, is 2-*o*-aldehydophenyl-3-*p*-dimethylaminophenylindone. C. S.

Some Anthrone Derivatives. E. WERTZ (*Annalen*, 1919, 418, 29—35).—2-Dimethylaminoanthrone is best obtained by heating 2-*p*-dimethylaminobenzoylbenzoic acid with 96% sulphuric acid for one hour at 65—70° (the higher limit must not be exceeded), pouring the cooled solution into water, and neutralising with sodium carbonate. When heated with benzaldehyde (1 mol.) in pyridine containing a few drops of piperidine in a sealed tube at 100°, or, less satisfactorily, with concentrated hydrochloric acid on the water-

bath, it yields 2-dimethylamino-10-benzylideneanthrone,



red needles, m. p. 173°. The latter in alcoholic solution is oxidised to 2-dimethylaminoanthraquinone by 5% hydrogen peroxide and 2*N*-sodium hydroxide. Benzylideneanthrone under similar conditions of oxidation yields anthraquinone and a substance, $\text{C}_{21}\text{H}_{14}\text{O}_2$, colourless crystals, m. p. 133°, which is possibly benzylidene-anthrone oxide, $\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C} \end{array} \begin{array}{c} \text{C}_6\text{H}_4 \\ \diagdown \quad \diagup \\ \text{CHPh} \end{array} \text{C}_6\text{H}_4 \text{CO}.$

C. S.

3-Methyluric Acid. HEINRICH BILTZ and MYRON HEYN (*Ber.*, 1919, 52, [B], 768—784).—It has been recently shown (Biltz and Heyn, A., 1917, i, 291) that δ -, α -, and ζ -methyluric acids are in reality 3-methyluric acid, a mixture of 3-methyluric acid with about 25% 9-methyluric acid and a mixture of 90% of the 3- with 10% of the 9-isomeride respectively. The present communication contains further data in this connexion.

Traube's acid is shown to be 3-methyluric acid, and his process affords the best means of preparing this substance.

The action of chlorine on 3-methyluric acid has been further studied with larger quantities of material; when moisture is carefully excluded, a crystalline 5(4)-chloro-3-methylisouric acid is obtained, which slowly decomposes above 150° and which is reduced by potassium iodide to 3-methyluric acid. Like the amorphous preparation previously described, it is converted by methyl and ethyl alcohols into the corresponding glycol ethers, m. p.'s 207° (decomp.) and 203° (decomp.) respectively. Attempts to convert it into 5(4)-alkyloxy-3-methylisouric acids or 3-methyluric glycol diethers were unsuccessful. It is converted by water into methyl-alloxan and carbamide, a reaction which is of interest, since it affords an explanation of the ready isolation of 5-chloro-9-methyl- ψ -uric acid from crude α -methyluric acid, the 3-methyluric acid in these circumstances being transformed into products which are readily soluble. In complete absence of moisture, chlorination of the " α "-acid proceeds differently, the 3-methyluric acid being converted into chloro-3-methylisouric acid, whilst 9-methyluric acid yields a product closely allied to the parent substance, probably either 4-chloro-9-methyl- $\Delta^{5:7}$ -isouric acid or 9-methyluric acid 4:5-dichloride.

Attempts are described to isolate 3-methyl- and 9-methyluric acids from " α -methyluric acid" by means of the chloropurines. The action of phosphoryl chloride appears to follow a similar course with each isomeride, and separation was not found possible by conversion into chloropurines and regeneration of the acids from these by means of hydrochloric acid. The chloropurines, however, could be separated by means of their barium salts. From the more sparingly soluble, 8-chloro-3-methylxanthine, decomposing at 344°, was obtained, whilst the more soluble salt yielded 2:6-dichloro-8-

hydroxy-9-methylpurine, decomposing at 275—276°. The latter is quantitatively converted by hydrochloric acid into 9-methyluric acid, but the corresponding yield of 3-methyluric acid is poor. The process affords further evidence of the nature of " α -methyluric" acid, but is without quantitative or preparative significance.

The solubility of derivatives of uric acid in boiling water is frequently described as a means of identification or differentiation. For this purpose, highly accurate values are not required provided that all determinations are performed in a uniform manner. The authors recommend the gradual addition of weighed amounts of finely powdered material to a known volume of water, which is kept gently boiling; the saturation point is regarded as attained when a permanent uniform turbidity appears through the whole solution.

H. W.

α -, ζ -, and δ -Methyluric Acids. HEINRICH BILTZ and MYRON HEYN (*Ber.*, 1919, **52**, [B], 784—804).—The three "isomeric" 3-methyluric acids have been recently examined by Billmann and Bjerrum (*A.*, 1917, i, 177), who have been led to conclusions differing somewhat considerably from those of Biltz and Heyn (*A.*, 1917, i, 291); the authors have therefore re-examined these acids and repeated much of the work of the Danish chemists. The chief results may be summarised as follows.

ζ -Methyluric acid differs from 3-methyluric acid. It is not a definite chemical compound, but consists rather of mixed crystals of 3-methyluric acid monohydrate and (about 5%) 9-methyluric acid monohydrate. In its properties it closely resembles 3-methyluric acid, but is slightly more soluble in water and rather more easily attacked by phosphoryl chloride.

α -Methyluric acid is also a mixture of 3- and 9-methyluric acids containing about 30—35% of the latter (that is, rather more than had been previously found). In no case is an equimolar compound formed. A crystallisation compound, possibly formed from two molecules of the 3-methyl acid and one molecule of the 9-methyl acid, together with two molecules of water of crystallisation, appears to be formed in small amount. This view is supported by the observation that α -methyluric acid, when crystallised by the method of Billmann and Bjerrum or by the authors' process, separates in large, shining platelets, which, when further crystallised, appear to be perfectly uniform. On the other hand, however, the relative proportion of the two isomerides seems to vary somewhat, and the water content is scarcely sufficiently constant for a definite chemical compound; in addition, the results of thermo-analytical investigation, which must be received with caution, are opposed to the idea of a compound. It is not at present possible to decide definitely between the two possibilities, mixed crystals or compound, but the authors incline to the former.

The increase in solubility due to admixture, and observed in some instances with α -methyluric acid, as compared with 3- and 9-methyluric acids, is interesting. Similar cases appear to have

been seldom investigated. The increased solubility of salicylic acid in the presence of dextrose, ethyl alcohol, and isobutyl alcohol has, however, been examined by Hoffmann and Langbeck (A., 1905, ii, 374), whilst Störmer, Grimm, and Laage (A., 1917, i, 647) have observed that stereoisomeric β -alkylcinnamic acids yield difficultly separable mixtures of lower solubility. H. W.

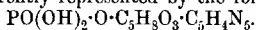
Substances which Inhibit the Coagulation of Proteins by Heat. G. MUNARETTO (*Arch. Pharm. experim.*, 1912, 460—468, 469—479; from *Bied. Zentr.*, 1919, 48, 128).—Formaldehyde and sulphurous acid are the most active inhibiting agents. Other reducing agents, arsenious acid, hydrogen sulphide, and sodium nitrite, are inactive. The addition of sulphurous acid or formaldehyde raises the viscosity of protein solutions. Ox serum becomes gelatinous on contact with sulphurous acid at the ordinary temperature. These effects suggest that a process of denaturation occurs. J. C. D.

Action of Acid and Alkali on Gluten. L. J. HENDERSON, EDWIN J. COHN, P. H. CATHCART, J. D. WACHMAN, and W. O. FENN (*J. Gen. Physiol.*, 1919, 1, 459—472).—Measurements of the hydrogen-ion concentration of solutions which had been in contact with powdered gluten show that the hydrogen-ion concentration in such systems is determined by the ratio of gluten to acid or base. The conclusion is reached that in systems containing gluten and acids or bases, the formation of salts, in accordance with the requirements of the mass law, is the fundamental phenomenon. Measurements were also made of the swelling and viscosity of the gluten component of such systems. The results indicate that simple chemical phenomena are most important in these systems, and that modifications of these, resulting from colloidal and heterogeneous characteristics, are of secondary importance in determining the condition of equilibrium, although somewhat more significant in the progress of the system toward the condition of equilibrium. J. C. D.

Steric Hindrance of Methyl Groups in the Nucleus. WOLFGANG HEUBNER (*Biochem. Zeitsch.*, 1919, 93, 395—396).—Certain aniline derivatives induce blood changes, with the formation of methæmoglobin, when administered to animals. This toxic action may be greatly reduced by the introduction of two methyl groups in the ortho-ortho- or the ortho-para-positions to the nitrogen group (compare A., 1913, i, 786). It is considered that the steric hindrance of the methyl groups prevents oxidation of the nitrogen group, which the author holds is necessary before methæmoglobin can be formed. J. C. D.

Adenine Mononucleotide. WALTER JONES and R. P. KENNEDY (*J. Pharmacol. Exp. Ther.*, 1918, 12, 253).—A crystalline

product, $C_{10}H_{14}O_7N_5P.H_2O$, has been prepared from yeast-nucleic acid. It is soluble in hot water, but very slightly so in cold. It gives the colour reactions for pentose and forms a brucine salt with two equivalents of brucine. Hydrolysis with dilute sulphuric acid yields adenine, but no guanine. Its entire phosphoric acid is readily split, so that it contains neither a cytosine nor a uracil group. It is apparently represented by the formula



J. C. D.

Amphoteric Colloids. II. Volumetric Analysis of Ion-Protein Compounds; the Significance of the Isoelectric Point for the Purification of Amphoteric Colloids. JACQUES LOEB (*J. Gen. Physiol.*, 1918, 1, 237—254).—At the isoelectric point, $p_H=4.7$, gelatin is practically not dissociated at all. By volumetric analysis, it has been shown that on the alkaline side of the isoelectric point gelatin can combine with cations only, whilst on the acid side it can combine with anions only. At the isoelectric point, gelatin (and probably amphoteric colloids generally) must give off any ion with which they are combined. The simplest method for obtaining these colloids approximately free from inorganic impurities would therefore seem to consist in bringing their hydrogen-ion concentration to that characteristic of their isoelectric point. When gelatin is in combination with univalent ions (Ag, Br, CNS), the curve representing the amount of ion-gelatin present is approximately parallel to the curves for swelling, osmotic pressure, and viscosity. This proves that the influence of the ions on these properties is determined by the chemical or stoichiometrical, and not by the "colloidal," properties. The sharp drop of these curves at the isoelectric point finds its explanation in the equal drop of the water-solubility of pure gelatin. It is not yet possible to state whether this is merely due to a lack of ionisation of gelatin or to the formation of a tautomeric or polymeric compound. A slight change in the hydrogen-ion concentration increases the water-solubility of gelatin near the isoelectric point. This is not produced by treatment with any other kind of univalent or multivalent ion, and it is considered that this is in harmony with a chemical conception of proteins rather than with the adsorption theory of colloids.

J. C. D.

Amphoteric Colloids. III. Chemical Basis of the Influence of Acid on the Physical Properties of Gelatin.

JACQUES LOEB (*J. Gen. Physiol.*, 1919, 1, 363—385. Compare preceding abstract).—The influence of hydrobromic acid on the physical properties of gelatin has a purely chemical or stoichiometrical basis. Gelatin is an amphoteric colloid which is sparingly soluble in water at its isoelectric point, whilst transformation into a salt with a univalent ion makes it soluble. Hence the curves representing the changes in osmotic pressure, viscosity, and swell-

ing of gelatin are approximately parallel to those representing the amount of bromine bound by the gelatin.

Titration with sodium hydroxide of gelatin, previously treated with hydrobromic acid, and therefore being on the acid side of its isoelectric point, results in the neutralisation of the pure gelatin (NaOH isoelectric) with sodium hydroxide, and besides in the neutralisation of the hydrobromic acid in combination with the gelatin.

J. C. D.

Amphoteric Colloids. IV. The Influence of the Valency of Cations on the Physical Properties of Gelatin. JACQUE LOEB (*J. Gen. Physiol.*, 1919, 1, 483—504. Compare preceding abstracts).—The amount of equivalents of metal in combination with 1 gram of a 1% gelatin solution previously treated with an alkali can be ascertained when the excess of alkali is washed away and the hydrogen-ion concentration determined. The results of experiments with lithium, sodium, potassium, ammonium, calcium and barium hydroxides show that twice as many univalent ions as bivalent cations combine with the same mass of gelatin.

The curves representing the influence of lithium, sodium, potassium, and ammonium on the osmotic pressure (and the other physical properties) of gelatin are identical, using p_H as abscissa. This contradicts the statements current in colloid chemistry, according to which these four cations have a different effect. The curves for calcium and barium gelatinates are also identical, but differ from those for the univalent metals examined. The ratio of the maximal osmotic pressures of the two groups is 1:3. This means that in a 1% solution of a metal gelatin there are approximately three times as many particles in solution or suspension when the metal is univalent as when it is bivalent.

The curves representing the conductivities of the same gelatin solutions are almost identical (for the same p_H).

The curves for the viscosity and swelling of barium or calcium and sodium gelatinates are approximately parallel to those for osmotic pressure. The practical identity of the conductivities of metal gelatinates with univalent and bivalent metals excludes the possibility that the differences observed in the osmotic pressure, viscosity, and swelling are determined by differences in degree of ionisation. If it is assumed that compounds of the type $\text{Ca}(\text{gelatin})_2$ exist, the two anions of which can form one aggregate of two gelatin anions, and that such aggregates can form larger aggregates of four, six, and eight gelatin anions, every one of which keeps its original charge, it would be possible to account for the phenomena observed.

J. C. D.

Physiological Chemistry.

Bioelements: The Chemical Elements of Living Matter.

INGO. W. D. HACKH (*J. Gen. Physiol.*, 1919, 1, 429—433).—The distribution of the elements which enter into the composition of living matter is considered with reference to a new periodic classification (Hackh, A., 1918, ii, 306, 396). J. C. D.

An Indicator Method of Measuring the Consumption of

Oxygen. W. J. V. OSTERHOUT (*J. Gen. Physiol.*, 1918, 1, 167—169).—The blood of *Limulus* when shaken with air absorbs oxygen and turns blue. In the presence of certain organisms which consume oxygen, it is quickly decolorised. A method is described for measuring the time required for the colour change, from which the rate of consumption of oxygen may be determined. J. C. D.

Chemical Studies in Physiology and Pathology. VI. The Biochemistry of Oxidation (Cell Respiration; Oxidising Enzymes; The Theory of Narcosis). E. HERZFELD and R.

LINGER (*Biochem. Zeitsch.*, 1919, 93, 324—352).—The atoms of the oxygen molecule can be activated by the formation of certain molecular compounds. In aqueous solution, oxygen may form a compound represented by the formula $\begin{array}{c} \text{H} \\ \diagup \quad \diagdown \\ \text{O} \cdots \text{O} \cdots \text{O} \\ \diagdown \quad \diagup \\ \text{H} \end{array}$.

This linking expresses the activity of the complex H_2O_4 . In this manner, complexes can be formed with water or metals in the form of peroxides. Oxygen bound in this manner can oxidise to carbon dioxide and water many organic substances, such as the lower fatty acids or their salts, without assistance.

The oxidative processes of the body are concerned with the oxidation of simple degradation products derived from the complex proteins, fats, and polysaccharides, and for this purpose the presence of oxygen in the activated form is sufficient. The assumption of the existence of special oxidising enzymes is superfluous. The relationship of these processes to narcosis and respiration is discussed. J. C. D.

The Presence of Calcium in the Red Blood Corpuscles of Ox and Man. DAVID MURRAY COWIE and HENRIETTA A.

CALHOUN (*J. Biol. Chem.*, 1919, 37, 505—509).—The red blood corpuscles contain calcium, but in a somewhat smaller concentration than the serum (compare Marriott and Howland, A., 1918, ii, 21). J. C. D.

Simultaneous Oxidation of Blood and of Dextrose.

R. FOSSE (*Compt. rend.*, 1919, 168, 908—910. Compare A., 1912, i, 541).—If, under suitable conditions, the proteins of blood and

dextrose are oxidised simultaneously, there is marked formation of carbamide. The yield of carbamide, formed by the oxidation of blood to which dextrose has been added, increases, within certain limits, with the proportion of dextrose and oxygen consumed. Under suitable conditions, the amount of carbamide formed may reach to 40 grams per litre of blood. W. G.

The Nutritive Value of the Wheat Kernel and its Milling Products. THOMAS B. OSBORNE and LAFAYETTE B. MENDEL [with the co-operation of EDNA L. FERRY and ALFRED J. WAKEMAN] (*J. Biol. Chem.*, 1919, **37**, 557—601).—The proteins of the entire wheat kernel are not greatly inferior for maintenance to caseinogen, edestin, or even to the total proteins of milk, but they are somewhat superior to gliadin. The wheat proteins considered in their entirety are sufficient for the growth of rats if consumed in sufficient amount. The quantity required is, however, relatively large when comparisons with proteins such as caseinogen are made.

The "crude protein" of commercial wheat embryo meal is more efficient for maintenance than that of the entire kernel or of the endosperm, and it is much more efficient for growth than endosperm protein. The protein of commercial wheat bran may be well utilised (70—75%) by the rat, and if eaten in sufficient amount may be considered somewhat superior to that of commercial embryo and decidedly superior to that of endosperm in promoting growth.

The proteins of the endosperm are adequate for maintenance, but inadequate for growth. Additions of meat, milk, and eggs to wheat flour greatly enhance the value of the proteins of the latter foodstuff for growth.

Commercial wheat embryo is rich in the water-soluble vitamins, but the pure isolated embryos do not appear to contain it. Evidence is given which indicates that the accessory factor is localised in the endosperm, although it is not uniformly distributed throughout it. No confirmation of the existence of a toxic substance in wheat has been obtained (compare Hart, Miller, and McCollum, A., 1916, i, 531).

The question of the degree to which wheat should be milled for general purposes is fully discussed, and the conclusion is reached that, except in special cases, little can be gained by including the bran and embryo in the flour when this is used under the dietary conditions prevailing in the United States. J. C. D.

The Origin of Formic Acid in the Organism. E. SALKOWSKI (*Zeitsch. physiol. Chem.*, 1919, **104**, 161—174).—Oxidation of glycerol with potassium permanganate in acid solution may yield as much as 24% of formaldehyde. An increased excretion of formic acid was observed to follow the administration of glycerol. It apparently arises by the intermediate formation of formaldehyde. Glycerophosphoric acid, choline, and lecithin all yield formaldehyde when oxidised by potassium permanganate in acid solution. There is no reason to suppose that the formic acid

excreted in the urine originates from one source. No doubt carbohydrates, glycerol, and lecithin all contribute a certain amount. 3% Hydrogen peroxide will oxidise lecithin, choline, and glycerophosphoric acid, with the formation of formaldehyde.

J. C. D.

Bioluminescence. VII. Reversibility of the Photogenic Reaction in Cypridina. E. NEWTON HARVEY (*J. Gen. Physiol.*, 1918, 1, 133—145).—The author has previously described two photogenic substances from the ostracod crustacean *Cypridina hilgendorffii*, photogenin, which is destroyed by boiling and is non-dialysable, and photophelein, which is stable to boiling and may be dialysed (A., 1917, i, 365). It is now suggested that photophelein is a mixture of two substances, one of which is an oxidisable substance similar to luciferin from *Pholas dactylus* (Dubois, A., 1897, ii, 112). Photogenin is now termed *luciferase*. The term photophelein is retained for a substance present in the extracts which acts by setting free bound or adsorbed luciferin. The action of this substance may be imitated by sodium chloride crystals or saponin. Luciferin is oxidised to *oxyluciferin*, and it is not believed that the change involves a fundamental destruction of the molecule, as it is a reversible process. The change is not analogous to that of hæmoglobin, for it cannot be reversed by reducing the partial pressure of the oxygen. It resembles more closely the oxidation of methylene-blue. The conception of Dubois that luciferin is formed from a precursor proluciferin by the agency of an enzyme coluciferase is held to be incorrect, and the correct explanation is believed to be that oxyluciferin may be reduced to luciferin by a reducing enzyme. Oxyluciferin will pass through a porcelain filter and is dialysable. Luciferin does not exhibit reducing properties similar to those of dextrose.

J. C. D.

Bioluminescence. IX. Chemical Nature of Cypridina Luciferin and Cypridina Luciferase. E. NEWTON HARVEY (*J. Gen. Physiol.*, 1919, 1, 269—293).—Of a large number of enzymes investigated, only those possessing a proteolytic activity had any digestive effect on luciferase, whilst none had any action on luciferin. A study was made of the "salting out" of luciferin and luciferase, as well as of their solubilities in various solvents, and their behaviour when treated with certain precipitants. Both substances are somewhat readily adsorbed by bone-black, kaolin, and colloidal ferric hydroxide. Consideration of the results obtained in this investigation leads to the opinion that luciferin is a protein on the border-line between the proteoses and peptones, whilst luciferase is regarded as being a more complicated protein, but not a globulin.

J. C. D.

Pharmacology of the Ureter. VI. Action of some Optical Isomerides. DAVID I. MACHT (*J. Pharmacol. and Exp. Ther.*, 1918, 12, 255—263).—*L*-Hyoscamine and *l*-hyoscine stimulate

the contractions of the ureter, whereas *d*-hyoscamine and *d*-hyoscyne have an inhibitory action. The action of atropine appears to be a summation of the action of the two optically active varieties. Inactive or racemic scopolamine shows an inhibitory action, which is ascribed to the preponderating effect of the *d*-component. *l*-Adrenaline is much more active in stimulating ureteral contractions and raising the tone of the ureters than the racemic variety. *d*-Adrenaline was not examined. *l*-Camphor produced a marked stimulation, but *d*-camphor was apparently inactive. The effect of the racemic form is represented by the arithmetical mean of the two components. J. C. D.

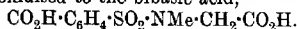
Isomerism and Anæsthetic Action. J. MORGENROTH (*Ber. Deut. pharm. Ges.*, 1919, 29, 233—250).—Comparison of the anæsthetic action of eucupine (*isoamylhydrocupreine*) dihydrochloride and *isoamylaphydroquinidine* dihydrochloride shows a quantitative difference between the activity of the stereoisomerides, the former being about twice as potent as the latter. Experiments with eucupine dihydrochloride and eucupinotoxin hydrochloride at different concentrations prove both structural isomerides to have anæsthetic action. The latter does not appear to depend on the intact quinclidine nucleus, since a pronounced increase in anæsthetising action is coincident with rupture of the carbon-nitrogen bond. The corresponding toxin is far more potent than eucupine, and forms the most powerful anæsthetic known (forty to fifty times stronger than cocaine). It has the power of producing prolonged anæsthesia.

The author is led to the conclusion that the chemotherapeutic action towards trypanosomes, the disinfecting action towards different bacteria, and the anæsthetic action are common to the quinotoxins and to the original alkaloids, and that comparatively all three functions are exerted to a greater degree by the latter. The difference in activity of ethylhydrocupreine and ethylhydrocupreinotoxin towards pneumococci appears to be an exception. Anæsthetic action does not appear to depend actually on space arrangement, since, as shown by the above experiments, the differences are only quantitative. In one instance quoted in the literature, that of benzoyltropeine and benzoyl- ψ -tropeine, a marked difference in anæsthetising action has been attributed to difference in spatial configuration; re-examination of these substances has failed to disclose any difference in their activity. H. W.

Secondary Action of Arsenic and Salicylic Acid Preparations on the Normal Stomach. BRUNO LEICHTENTRITT (*Zeitsch. physiol. Chem.*, 1919, 104, 154—160).—According to Klossman (*A.*, 1912, ii, 965), sodium salicylate causes a decreased secretion of gastric juice. This was not confirmed, for it was found that aspirin, sodium salicylate, and salol caused an increased flow. His results with Fowler's solution (liq. potass. arsenic) are, however, confirmed. This preparation, as well as certain organic arsenic

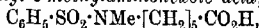
preparations, such as elarson and arsacetin, increased the flow of gastric juice. A similar result was obtained by the administration of preparations containing both iron and arsenic. J. C. D.

A New Instance of β -Oxidation in the Animal Body. KARL THOMAS and HERBERT SCHOTTE (*Zeitsch. physiol. Chem.*, 1919, 104, 140—153).—Oral administration of *p*-toluenesulphonylsarcosine to rabbits results in 80% being excreted in the urine unchanged; 4% is oxidised to the bibasic acid,



81% of benzenesulphonylsarcosine administered in the same manner was recovered from the urine.

ϵ -Benzenesulphonyl- ϵ -methylaminohezoic acid,



prepared from ϵ -methyl-leucine, crystallises from methyl formate and light petroleum in slender, white needles, m. p. 57°. When administered to rabbits, 44% was recovered from the urine as γ -benzenesulphonylmethylaminobutyric acid, oxidation having occurred at the β -carbon atom.

Benzenesulphonylmethylaminobutyric acid, $\text{C}_6\text{H}_5\cdot\text{SO}_2\cdot\text{NH}\cdot[\text{CH}_2]_3\cdot\text{CO}_2\text{H}$, m. p. 91—92°. When methylated with methyl sulphate, it yields *benzenesulphonylmethylaminobutyric acid*, m. p. 84—87°. This substance was recovered unchanged from the urine after administration to rabbits. J. C. D.

Detoxication of Inhaled Hydrogen Cyanide by Sodium Thiosulphate. E. TEICHMANN and W. NAGEL (*Biochem. Zeitsch.*, 1919, 93, 312—323).—The observation of Lang (*Arch. exp. Path. Pharm.*, 1895, 36, 75) that sodium thiosulphate can protect animals against the toxic effects of hydrogen cyanide is confirmed. The salt is efficient as an antidote when the poison is inhaled by animals. It will be necessary to establish that sodium thiosulphate is not toxic for man before the therapeutic application can be made. J. C. D.

Chemistry of Vegetable Physiology and Agriculture.

Influence of Different Agents on the Saccharifying and Fermenting Powers of *Mucor* Boulard. BETTINGER and DELAYALE (*Bull. Assoc. Chim. Sucr.*, 1918, 35, 114—129).—In experiments on the cultivation of *Mucor Boulard* on sugared extract of malt combs, the development of acid was found to be in direct proportion within limits to the access of air and the sugar content. Comparatively low temperatures gave the highest results. Succinic acid is the only non-volatile acid formed, whilst acetic acid mainly constitutes the volatile acidity. Nitrogenous matter

at first retards, but later accelerates, saccharification, peptone and asparagine giving the best results, whereas ammonium sulphate has a comparatively slight effect in this direction. Calcium and potassium phosphates, and to a less degree ammonium phosphate, accelerate saccharification, but sodium phosphate produces little or no result.

J. P. O.

The Sensitiveness of Living Yeast to H^+ and OH^- Concentration. H. VON EULER and F. EMBERG (*Zeitsch. Biol.*, 1919, 69, 349—364).—Fermentation by the living cell is not effected solely by zymase, but is bound up to a large extent with the life of the cell itself. From the investigation of a bottom yeast, it is shown that the sensitiveness to acid and alkali of the process of inversion by the living yeast cell is not appreciably different from the sensitiveness of the isolated enzyme. It is therefore possible to conclude that the enzyme exists in the free state in the cell. The influence of growing the bottom yeast at different hydrogen-ion concentrations (p_H 3.5—3.8 and 6.6—7.2) on the characteristic cellular activities has been studied. The inverting action was little affected, but appreciable changes in the rate of growth and composition of the cells were noted.

J. C. D.

Changed Course of Alcoholic Fermentation in an Alkaline Medium. ALICE OELSNER and ALFRED KOCH (*Zeitsch. physiol. Chem.*, 1919, 104, 175—181).—The authors have failed to confirm the statements of Wilenko (A., 1917, i, 680) that the course of the fermentation of sugar in an alkaline phosphate medium is changed and that no carbon dioxide is formed under those conditions. The alkalinity delays the fermentation, but alcohol and carbon dioxide are always obtained. The observation of Neuberg and Färber (A., 1917, i, 502) that more aldehyde is produced when the fermentation is conducted in an alkaline medium is confirmed.

J. C. D.

The Temperature-coefficient of Photosynthesis. W. J. V. OSTERHOUT and A. R. C. HAAS (*J. Gen. Physiol.*, 1919, 1, 295—298).—The temperature-coefficient of photosynthesis in *Utricularia rigida* between 17° and 27° is 1.81. It is suggested that photosynthesis involves catenary reactions of the type $S \rightarrow M \rightarrow P$, in which S represents a substance which, under the influence of light, breaks down to form M ; this in turn forms P , the amount of which is proportional to the amount of photosynthesis. If the reaction $S \rightarrow M$ is more rapid than $M \rightarrow P$, the speed of the reaction as a whole will depend chiefly on the speed of the change $M \rightarrow P$.

The effect on the whole reaction of a rise of temperature will therefore depend chiefly on its effect on the second reaction. It is therefore not surprising to find a high temperature-coefficient for photosynthesis. Analogous cases exist in photochemistry.

J. C. D.

Permeability in Plants. W. J. V. OSTERHOUT (*J. Gen. Physiol.*, 1919, 1, 299—304).—Certain conclusions concerning the behaviour of protoplasm drawn from the results of experiments on *Laminaria Agardhii* (compare A., 1918, i, 470) have been confirmed by experiments with a red alga (*Rhodymenia palmata*), a green alga (*Ulva rigida*), and a flowering plant (*Zostera marina*).
J. C. D.

Decrease of Permeability and Antagonistic Effects caused by Bile Salts. W. J. V. OSTERHOUT (*J. Gen. Physiol.*, 1919, 1, 405—408).—The results of experiments on the electrical conductivity of *Laminaria* indicate that sodium taurocholate is able to produce a decrease in permeability and to antagonise sodium chloride. This confirms the hypothesis that antagonistic relations can be predicted from studies on the permeability of pure substances.
J. C. D.

A Comparison of Permeability in Plant and Animal Cells. W. J. V. OSTERHOUT (*J. Gen. Physiol.*, 1919, 1, 409—413).—The author has made quantitative studies of the permeability of plant cells as represented by *Laminaria*, and animal cells as represented by the skin of frogs (*Rana pipiens*). Both tissues showed a closely similar behaviour, and this agreement indicates that the conclusions drawn from a study of *Laminaria* are of general application. It would appear that the physiological characteristics brought to light by these studies belong to the fundamental properties of protoplasm.
J. C. D.

Effect of certain Compounds of Barium and Strontium on the Growth of Plants. J. S. MCHARGUE (*J. Agric. Res.*, 1919, 16, 183—194).—Barium or strontium carbonate in the absence of calcium carbonate is toxic to plants, the former having a greater toxicity than the latter, but in the presence of calcium carbonate they appear to exert a distinct stimulating influence on the growth of the plants studied. Barium sulphate is much more toxic than barium carbonate. Neither barium nor strontium can replace calcium as a plant food. The root growth is accelerated in all cases where barium or strontium carbonate is added to the sand in which the plants are growing.
W. G.

The Identification, Localisation, and Distribution of Oxalic Acid [Soluble Oxalates] in Plants. NORBERT PATSCHOVSKY (*Ber. Deut. bot. Ges.*, 1918, 36, 542—548).—The usual method of detecting the presence of soluble oxalates in cell sap by means of potassium salts suffers under the disadvantages that the potassium oxalate crystals are not very characteristic, and that they are liable to be completely obscured by co-precipitated tannins. The author finds ferrous sulphate or ferrous ammonium sulphate to be a more suitable reagent; the not too thin section is immersed on an object-glass in an acetic acid solution of the ferrous salt (10%), covered

with a slip, and gently warmed to expel air; in the presence of oxalates, ferrous oxalate separates after a time in crystals, the size of which is about $15 \times 9 \mu$. Larger crystals may be obtained by delaying the separation by addition of sodium acetate, sucrose, or gelatin.

The localisation of oxalates is best effected by injecting a highly concentrated ferrous solution into the plant by means of an air pump; under these conditions, precipitation of ferrous oxalate occurs within the cell, whilst with less concentrated solutions the oxalates diffuse through the cell wall, and precipitation takes place in the intercellular region.

The ferrous reagent has the further advantage of allowing a simultaneous detection of tannins.

The author has applied the method to a large number of plants; for details, the original paper must be consulted. H. W.

Action of Coal Gas on Plants. V. Action on Trees. Hydrocyanic Acid as the most Detrimental Constituent of Gas. C. WEHMER (*Ber. deut. Bot. Ges.*, 1918, **36**, 460—461. Compare A., 1917, i, 618; this vol., i, 114).—Continuing his previous experiments on the action of coal gas on the root systems of trees, the author now finds that in many instances in which the detrimental action is not immediately apparent, the effects are observed at the end of the period of winter rest, when in almost every instance the tree is killed. The most detrimental constituent of coal gas is now proved to be hydrogen cyanide; the toxicity of gas-water is shown to be exactly similar to that of a hydrocyanic acid solution of equivalent concentration, and, further, the violent toxic action of coal gas is not observed if the gas is passed through a solution of alkali hydroxide and ferrous sulphate. Cress is extraordinarily sensitive to minute traces of hydrocyanic acid. H. W.

A Purely Mineral Solution Capable of Assuring the complete Evolution of Maize Cultivated and Sheltered from Bacteria. P. MAZÉ (*Ann. Inst. Pasteur*, 1919, **33**, 139—173).—From a series of water-culture experiments, the author finds that, in addition to nitrogen, phosphorus, potassium, calcium, magnesium, sulphur, iron, chlorine, silicon, manganese, and zinc, boron, aluminium, fluorine, and iodine are equally essential to the development of maize. Organic substances, excluding the organic reserves of the seed, although not indispensable, exert a beneficial influence on the growth of the plant when added to the mineral nutrient solution. It is advisable that the iron should be present in the ferric state in the culture solution, or that some oxidising agent should be present. Insufficient aeration of the culture solution exerts an unfavourable influence on the vegetation. W. G.

General and Physical Chemistry.

Relation between Intensity of Tyndall Beam and Size of Particles. RICHARD C. TOLMAN, ROSCOE H. GERKE, ADIN P. BROOKS, ALBERT G. HERMAN, ROBERT S. MULLIKEN, and HARRY DE W. SMYTH (*J. Amer. Chem. Soc.*, 1919, **41**, 575—587).—The intensity of the Tyndall beam in rosin smokes has been investigated further by the method previously described (this vol., ii, 180). In the case of smoke, since the particles are not of uniform size, no attempt was made to measure the size of the particles, but the results show that for the range of particles 10^{-6} — 10^{-4} cm., the Tyndall-meter reading increases with increased dispersion. Suspensions of silica particles in water were prepared, and the intensity of the Tyndall beam in these suspensions investigated. The particles were of uniform size and varied in the different suspensions from 10 — 260×10^{-5} cm. The Tyndall-meter readings in the case of silica suspensions increase with decreasing diameter of the particles. The results show that the readings are closely proportional to the reciprocal of the diameter of the particles. The relationships between the readings (T) and size of the particles are given by the equations $T = knd^6$ for very small particles and $T = k^1nd^2$ for large particles; d is the diameter of the particles, n the number of particles per c.c., and k and k^1 are constants. When the total concentration of the suspensions is given by c ; $c \propto nd^3$, hence the equations may be written $T = kcd^3$ and $T = k^1c/d$. J. F. S.

Absorption by Troubled Media. Application to the Estimation of Suspensions. CHARLES CHÉNEVEAU and RENÉ AUDUBERT (*Compt. rend.*, 1919, **168**, 766—768).—The authors deduce the formula $1 - I/I_0 = e^{-B/M^\beta}$, where I/I_0 is the coefficient of transmission of light of the fine suspension, M is the total mass of particles, and B and β are two constants dependent only on the nature of the particles in suspension and the wave-length of light used. The accuracy of this formula has been verified for certain heterogeneous suspensions of mastic and for suspensions of silver chloride and barium sulphate. This thus provides a method of determining the amount of material in suspension providing there is no immediate sedimentation. W. G.

Conductivity and Absorption of Sodium Vapour. ADOLFO CAMPETTI (*Nuovo Cim.*, 1918, [vi], **16**, ii, 115—138).—The results of the author's experiments show that, in unsaturated sodium vapour kept in the dark and freed from electrons emitted from the surface of the fused metal, spontaneous ionisation in the volume of the vapour occurs at high temperature; this ionisation becomes clearly manifest above 400° without marked dissymmetry as regards

the sign of the disperse charge. Such conductivity in the volume of the vapour is closely connected with the commencement of the absorption of the *D*-line, which under the above conditions is observed only at about 430°, but then persists when the temperature falls considerably. The cause of the appearance of absorption at somewhat lower temperatures under the ordinary conditions of observation is clearly shown to be the presence of electrons either given off from the surface of the molten metal or arising from the atoms of the metal in the state of vapour as a result of photo-electric action. It appears probable that the emitting or absorbing vibrators in sodium vapour are, for the *D*-line, the positive atom ions.

T. H. P.

Spectrum of Neon. K. W. MEISSNER (*Ann. Physik*, 1919, [iv], 58, 333—374).—The red and infra-red spectrum of neon has been investigated by the interferometric method of Fabry and Perot (*Ann. Chim. Phys.*, 1897, [vii], 12, 459), and also by means of a concave grating of 1 metre radius. Some seventy-five lines are recorded between the wave-lengths 7051.314 and 9840.42 Å.U., and in all cases the vacuum wave-length is calculated. The wave-lengths of the present measurements, together with those of previous measurements of the other portions of the spectrum, are examined with the object of arranging them in series, and the relationships of the eight series groups calculated. J. F. S.

The Constitution of the Atom and the Properties of Band Spectra. H. DESLANDRES (*Compt. rend.*, 1919, 168, 861—868).—Vegard's work (compare A., 1918, ii, 93, 94, 144) gives data concerning the inner rings of electrons adjacent to the nucleus, and the author considers that a study of band spectra may throw some light on the composition of the outer rings. The edges of the bands, which form the structure of the spectra, are given by $\nu = B(n + \beta)^2/2 - C'(p + \gamma)^2/2 + K$, where B , C , K , β , and γ are constants, n and p being successive whole numbers.

The three types of spectra, line, band, and X-ray, are due to the action, more or less strong, of ions and electrons which encounter the atom. If the electron which arrives is very rapid, it penetrates to the nucleus and disarranges the ring nearest to the nucleus, causing it to lose an electron and giving rise to X-rays. If the electron is less rapid, only an outer ring is disarranged, and the line spectrum results. If, however, the velocity of the approaching electron is still less, the atom is only deformed and emits the band spectrum.

W. G.

The Verification of Bohr's Atomic Theory of Optical Spectra by Investigations of the Non-elastic Collisions of Slow Electrons with Gas Molecules. J. FRANCK and G. HERTZ (*Physikal. Zeitsch.*, 1919, 20, 132—143. Compare *ibid.*, A., 1914, ii, 515; 1916, ii, 461).—The principle that for the monatomic gases without affinity for electrons the electrons are reflected from the

atoms with perfect elasticity up to a critical velocity of collision, when they lose their total energy of translation and give rise to radiation, has been found to be in complete accord with Bohr's theory. The critical energy of the electron in the case of mercury vapour, derived from a potential difference of 4.9 ± 0.1 volt, is equal to $h\nu$, where h is the quantum and ν the frequency corresponding with 2536 \AA . in the ultra-violet spectrum of mercury. The absorption and emission lines can be excited by free electrons, which suffer a loss of energy of $h\nu$ on collision. For normal, not excited, atoms, the change of the electron from one steady orbit to another corresponds with the absorption spectrum series. The limit of frequency of the series in the ultra-violet multiplied by the quantum h gives the work done in ionising the atom, and the limit may be calculated from the ionising potential and vice versa. The investigation of inelastic electronic collision and its attendant light emission gives a new means of analysing the lines of a spectrum into series and determining their relation. F. S.

Explanation of the Röntgen Spectrum and the Constitution of the Atom. L. VEGARD (*Physikal. Zeitsch.*, 1919, 20, 97—104).—A theoretical paper in which the main results of previous publications are summarised (*A.*, 1918, ii, 93, 94, 144). A generalised frequency formula is developed on the basis of the preceding work, and this is tested by comparison of curves produced from results calculated by this formula with the corresponding experimental curves. J. F. S.

X-Ray Spectroscopy. The L-Absorption Spectrum of Radium. M. DE BROGLIE (*Compt. rend.*, 1919, 168, 854—855).—The L-absorption band of radium has been obtained by passing a beam of X-rays through a glass capillary tube containing solid radium sulphate. The tube is fixed before the spectroscopic slit. The wave-length $\lambda = 0.659 \times 10^{-8} \text{ cm.}$ is found for this band, and calculations from this value lead to 88 as the atomic number of radium. J. F. S.

Crystalline Structure of Alums and the Rôle of Water of Crystallisation. L. VEGARD (*Ann. Physik*, 1919, [iv], 58, 291—296).—Polemical against Schaefer and Schubert (*A.*, 1916, ii, 505). The author shows that the measurements of Schaefer and Schubert do not prove that water of crystallisation occurs as a structural component in the grating system, and that the claim for priority made by these authors is unfounded. J. F. S.

Optical Investigation of the Constitution of some Oxygen Acids of Chlorine and Bromine and of their Esters and Salts. KONRAD SCHAEFER and WILLY KÖHLER (*Zeitsch. physikal. Chem.*, 1919, 93, 312—324).—The absorption spectra of a number of the oxygen acids of the halogens, their esters, and salts have been measured. In the case of hypochlorous acid, ethyl hypo-

chlorite, and several metallic hypochlorites it is shown that the acid and ester have identical absorption spectra, but when the acid is completely neutralised by sodium hydroxide, the absorption spectrum changes in the sense that a deep, well-defined, broad band appears. Incomplete neutralisation gives an absorption spectrum which indicates both acid and salt. The author puts forward the formula $\text{Cl}\cdot\text{OH}$ and $\text{Cl}\cdot\text{OEt}$ for the acid and ester

respectively, and $\text{Cl}\cdot\text{O}\cdot\text{Na} = \text{Cl}\cdot\text{O} + \text{Na}^+$ for the salt. Hypobromous acid and sodium hypobromite give absorption spectra similar to those of the corresponding chlorine compounds. Solutions of chlorine dioxide, chlorous acid, and several chlorites were also examined. Gaseous chlorine dioxide shows a broad band and a large number of narrow bands, whilst on solution the bands are broadened and many run together, but in general the region of absorption remains the same. The maximum of absorption is at 2900, and the minimum at the frequency 3800. These results indicate that there is little formation of chloric or chlorous acid on solution. On neutralisation, the band disappears, so that the chlorites have a different constitution from the acid, the formulae

$\text{O}=\text{Cl}\cdot\text{OH}$ and $\text{Cl}\cdot\text{O}\cdot\text{M}$ being suggested in the two cases. Bromic acid, iodic acid, and their alkali salts were also investigated. The only difference observed in these cases was the shifting of the terminal absorption toward higher frequencies in the case of the bromine compounds. The measurements show that the constitution of these acids is probably that of a true acid, as distinguished from a pseudo-acid.

J. F. S.

Use of Einstein's Photochemical Equivalent Law. I. W. NERNST (*Zeitsch. Elektrochem.*, 1918, **24**, 335—336).—A theoretical paper in which the reason for the inapplicability of the Einstein photochemical law to the photosynthesis of hydrogen chloride is put forward. The primary action of light is the splitting of the chlorine molecule, this then reacts $\text{Cl} + \text{H}_2 = \text{HCl} + \text{H} + 25,000$ cal., and the hydrogen atom thus produced reacts with a chlorine molecule, $\text{H} + \text{Cl}_2 = \text{HCl} + \text{Cl} + 19,000$ cal. This explains why so much more hydrogen chloride is produced than correspond with the requirement of the Einstein law. This also explains the negative catalytic effect of impurities on this reaction. The chlorine and hydrogen atoms are very reactive substances, and consequently will be removed from the reaction system by their combination with the impurities. This view is confirmed by the limited reaction when bromine vapour and hydrogen are illuminated, for, as the equation $\text{Br} + \text{H}_2 = \text{HBr} + \text{H} - 15,000$ cal shows, hydrogen is not a suitable acceptor for bromine.

J. F. S.

Use of Einstein's Photochemical Equivalent Law. II. LOTTE PUSCH (*Zeitsch. Elektrochem.*, 1918, **24**, 336—339. Compare preceding abstract).—The reaction between bromine vapour

and hydrogen in the presence of toluene, hexane, and heptane when exposed to light has been investigated. The results confirm the view put forward in the preceding paper that in the case of chlorine and hydrogen the primary reaction is strictly in accordance with the Einstein law, and that the secondary reactions account for the extremely large quantities of hydrogen chloride produced.

J. F. S.

The Possibility of Separating Isotopes. F. A. LINDEMANN and F. W. ASTRON (*Phil. Mag.*, 1919, (vi), **37**, 523-534).—The possible methods of separating isotopes, distillation, to which, thermodynamically, chemical separation is closely allied, diffusion, density, and positive rays, are discussed theoretically. The conclusion is reached that separation by distillation and chemical methods ought to be possible under appropriate conditions, although the separation may be small. None of the possible physical methods holds out any prospect of effecting an easy separation, centrifugal separation being the most promising. For neon and meta-neon, with a peripheral velocity of 10^5 cm. per second, it is calculated that the apparent atomic weight of the gas at the edge should be 1.0065 times that of the gas at the centre, and for thorio- and uranio-lead a nearly 50% increase in the concentration of the former at the edge might result.

Experiments are described on the fractionation of atmospheric neon by charcoal at liquid air temperature. After about 3000 fractionations, in which the gas was divided into seven main fractions, the density as determined by the quartz micro-balance was unchanged.

F. S.

Protactinium and the Life Period of Actinium. OTTO HAHN and LISE MEITNER (*Physikal. Zeitsch.*, 1919, **20**, 127-130. Compare *ibid.*, A., 1918, ii, 345; Soddy and Cranston, A., 1918, ii, 211).—Evidence of the period of actinium obtained from the proportionate increase of the α -radiation of protactinium preparations with time confirms the value obtained directly from the rate of decay of the radiation of actinium preparations. From the known ranges of the six α -rays involved in the protactinium-actinium series, the ratio of the initial ionisation produced by a thin film of protactinium to that when the actinium and its products are in equilibrium with the protactinium is calculated to be 1.574. From the proportionate increase of α -radiation of five preparations over periods from 400 to 600 days, a half-period of actinium of twenty years is deduced. This indicates that in the carbon tetrachloride sublimation of Soddy and Cranston less than 1% of the eka-tantalum (protactinium) in the mineral was separated. The value found from the decay curve of the radiation of actinium over seven years gives for the half-period of actinium twenty years ($\pm 10\%$). This corresponds with a period of average life of 38.8 years.

F. S.

Chemical Action produced by Radium Emanation. I. Combination of Hydrogen and Oxygen. S. C. LIND (*J. Amer. Chem. Soc.*, 1919, **41**, 531—551).—The velocity of combination of hydrogen and oxygen under the influence of radium emanation has been investigated. The experiments were effected in spherical and cylindrical bulbs of varying size by a method which is a slight modification of that of Cameron and Ramsay (T., 1908, **93**, 966—992). It is shown that the velocity of reaction in a given volume is dependent on two variables only, the quantity of emanation, E , and the gas pressure, P . The velocity constant obtained by integration of the equation arising from this assumption has been verified. It has the form $(\log P/P_0)/E_0(e^{-x} - 1) = \text{const.}$ The effect of increasing the spherical volume is to diminish the velocity constant (expressed in terms of pressure) according to the equation $84 \cdot 1/D^2 = \text{const.}$, where D is the diameter in cm. This is to be expected from the increase of the average path of the α -particle proportional to D , whilst the pressure effect diminishes proportionally to D^3 . The above formula is applicable only to globes in which the size of the shortest α -ray is not exceeded by the diameter. Varying proportions of hydrogen and oxygen change the velocity in the way which is to be expected from the change produced in the specific ionisations. Excess of oxygen gives a velocity higher than normal, which increases as the proportion of oxygen increases. Excess of hydrogen produces the opposite effect. The temperature-coefficient of the reaction between 0° and 25° is zero, as would be expected from ionisation. Calculation of the ionisation by the method of average path of the α -particles shows that for each pair of ions produced in the gaseous mixture, 3.9 molecules of water are formed: this value agrees fairly well with 3.7 found by Scheuer (A., 1914, ii, 762). The reaction in cylindrical volumes obeys the same laws as that in spherical volumes, which would appear to confirm the author's original contention that the average path in a cylinder is the same as in a sphere of equal volume (*Amer. Electrochem. Trans.*, **34**). J. F. S.

Chemical Action produced by Radium Emanation. II. Chemical Effect of Recoil Atoms. S. C. LIND (*J. Amer. Chem. Soc.*, 1919, **41**, 551—559. See preceding abstract).—The action of radium emanation in causing the combination of electrolytic hydrogen and oxygen is abnormally high in small spheres, particularly at low gaseous pressures. The action is shown to be six to seven times greater than that due to the normal α -ray effect. This abnormally high velocity is explained by the assumption that the recoil atoms contribute to the reaction in proportion to their relative ionising power. The results of the author's calculations and experiments are in general agreement with Wertenstein's ionisation data for recoil atoms (A., 1914, ii, 514). J. F. S.

Determination of the Ionisation Potential for Electrons in Helium. FRANK HORTON and ANN CATHERINE DAVIES (*Proc. Roy. Soc.*, 1919, [A], **95**, 408—429).—The ionisation potential of

electrons generated by a heated tantalum wire in helium of low pressure has been experimentally determined. The experiments show that radiation occurs when electrons having a velocity of about 20.5 volts collide with helium atoms, and that this is not accompanied by any ionisation of the gas. It is also shown that ionisation of the helium occurs when the velocity of the electrons is raised to about 25.7 volts, and that no other type of radiation is produced at this point. The potential values were obtained from an accurate investigation of the position of the bends of the current-potential difference curves over a range of 2—3 volts in the neighbourhood of the value. The mean values from these experiments were 20.4 volts and 25.7 volts respectively. By a method in which the value of V_3 was made zero, and the electrons could produce radiation or ionisation over longer paths, the mean values 20.45 volts and 25.5 volts were obtained. It may be taken that 20.4 volts represents the minimum radiation potential and 25.6 volts the minimum ionisation potential. These values confirm Bohr's suggestion that radiation, and not ionisation, occurs at about 20 volts, but the value found for the ionisation potential is considerably lower than the value, 29 volts, deduced from Bohr's theory of the structure of the helium atom.

J. F. S.

Molecular Electric Field in Gases. P. DEBYE (*Physikal. Zeitsch.*, 1919, 20, 160—161).—A theoretical paper in which calculations, based on the Stark hypothesis that the broadening of spectral lines is to be attributed to a molecular electric field, are made by which the approximate dimensions of the molecular electric field are calculated. Assuming that the charge of an electron is 5×10^{-10} g.¹ cm.¹ sec.⁻¹ (electrostatic units), and the radius of the molecule is 10^{-8} cm., it is shown that the charge on a charged molecule or ion may be taken as 5×10^{-10} g.¹ cm.¹ sec.⁻¹, and in the case of an uncharged molecule which bears an electric moment, this may be put at 5×10^{-13} g.¹ cm.¹ sec.⁻¹. If the electric moment disappears, the electric moment of inertia is then calculated to 5×10^{-26} g.¹ cm.¹ sec.⁻¹. Values of the above dimensions have been recently obtained by Jona (this vol., ii, 130). The value of the field strength due to the ions (F_1) is given by $F_1 = en^2$, where e is the ionic charge and n the number of gas molecules per cubic centimetre. The field strength, F_2 , due to uncharged molecules which have an electric moment, is given by $F_2 = mn$, where m is the electric moment, and for the case where the electric moment is zero and only an electric moment of inertia is present, $F_3 = \Theta n^2$ gives the field due to this cause, where Θ is the electric moment of inertia. Substituting the appropriate data $F_1 = 4500$ electrostatic units = 1,350,000 volts/cm., $F_2 = 135$ electrostatic units = 40,500 volts/cm., and $F_3 = 4$ electrostatic units = 1200 volts/cm. In the case of ammonia and sulphur dioxide, the electric moment is actually of the above order, and an electric field of 4×10^4 volts/cm. is existent.

J. F. S.

Electromotive Activity of Carbon Monoxide. FRIEDRICH AUERBACH (*Zeitsch. Elektrochem.*, 1919, 25, 82—84).—A theoretical paper in which the activity of carbon monoxide in electromotive processes is considered. It is shown that the *E.M.F.* given by Hofmann (this vol., ii, 8) for the element O_2/CO may not be directly compared with that calculated from the free energy of the reaction $2CO + O_2 = 2CO_2$, because in alkaline electrolytes carbon monoxide is not burnt to carbon dioxide, but to carbonate. In the present calculations, the *E.M.F.* is much smaller than that observed by Hofmann. J. F. S.

A Modified Hydrogen Electrode. J. HUDIG and W. STURM (*Chem. Weekblad*, 1919, 16, 473—481).—In their measurements of the hydrogen-ion concentration of aqueous soil extracts by means of the hydrogen electrode, the authors experienced difficulty in obtaining constant results for any one extract, even after filtration of the latter through an ultra-filter. Whilst no explanation of the observed fluctuations in *E.M.F.* is suggested, it is found possible to obtain satisfactory constancy in the readings by the following modifications in the construction and use of the hydrogen electrode. The electrode consists of a platinum gauze cylinder platinised over a gold coating. The soil suspension is contained in a closed vessel, through the stopper of which pass the electrode, gas inlet and outlet tubes, electrolyte tube, and a stirring gear motor driven through a mercury seal. A rapid stream of hydrogen is supplied both to the inner and to the outer surface of the gauze cylinder during the measurement, whilst soil and liquid are kept in intimate contact by vigorous stirring. W. S. M.

The Theory of Electrolytic Ions. IX. Space filling and Mobility of Univalent Organic Ions. R. LORENZ (*Zeitsch. anorg. Chem.*, 1919, 105, 175—186).—The author has calculated the space-filling numbers of more than one hundred univalent organic cations, containing from 6 to 44 atoms (compare A., 1918 ii, 303). The space-filling number ψ is the ratio of two volumes ϕ/V , where ϕ is the ionic volume calculated from the ionic mobility and V is the volume derived from the density or from Kopp's formula. The ion radius, r , is given by the formula $r = 1/\psi \times 8.954 \cdot 10^{-7}$. In the series of ions examined, this radius is found to be a linear function of the number of atoms in the ion. Hevesy (A., 1916, ii, 594) has advanced the theory that the ions in solution endeavour to attain an approximately constant potential, which, in the case of water, is about 70 millivolts. The normal radius of an ion charged to this potential he calculates to be 2.8×10^{-8} cm. To adjust their potential, the smaller ions, he supposes, increase their radius by becoming hydrated, thereby lowering their mobility. In the series of ions under examination this "normal" radius, corresponding with a "normal" mobility, is reached with not fewer than 27 atoms in the ion. According to Hevesy's theory, ions with fewer than 27 atoms should become

hydrated to bring their radii and mobilities to the "normal" value. There is no evidence that they do become so hydrated, however, for the relation between the number of atoms and the ionic radius is linear, and there is no discontinuity in the curve at about 27 atoms. Further, there is very little difference between the mean values of the space-filling numbers with more than 27 atoms ($\psi=0.474$) and the mean of all ions with from 6 to 44 atoms ($\psi=0.388$). For the "ideal" organic cation containing between 4 and 50 atoms, the value of the space-filling number can be taken as 0.40.

E. H. R.

Movement of the Ions during Electrolysis. CARLO DEL LUNGO (*Nuovo Cim.*, 1918, [vi], 16, ii, 173—181).—By application of Stokes's law to the question of the movement of the ions, the author deduces theoretically Walden's empirical law, according to which, for one and the same electrolyte, the product of the viscosity of the solvent and of the equivalent conductivity, Λ_0 , is a constant magnitude independent of the temperature. It is found also that the variation of the conductivity, Λ_0 , should depend solely on the variation of the viscosity-coefficient, η , as it may be assumed that, at least within certain limits, change of temperature does not sensibly influence the diameters of the ions. Consequently, the temperature variation of Λ_0 should be virtually the same for all electrolytes in aqueous solution. Not only is the law in general verified for salts, but the temperature-coefficients of conductivity between 18° and 40° have the limiting values $2.3.10^{-12}$ and $2.6.10^{-12}$, which correspond closely with the temperature-coefficient of the viscosity of water.

Stokes's law allows also of calculation of the diameter of the ions, and the values thus derived are in good agreement with those deduced in accordance with the kinetic theory of gases. In general, the ions are small in comparison with the molecules, but the difference is exceptionally marked with the ions H^+ and OH' , the diameters of which are only about one half of what they should be according to the diameters of the molecules H_2 , O_2 , and H_2O . The existence of free H^+ and OH' ions in all aqueous solutions, and perhaps in greater number in solutions of acids and bases, would cause the calculated velocities of the ions of the electrolyte to be greater than the true values; these considerations would explain the exceptionally high values obtained for the transport velocities of the ions H^+ and OH' and the low values of the corresponding temperature-coefficients, and of the diameters calculated according to Stokes's law. It appears that the ions H^+ and OH' exist under special conditions different from those shown by other ions, and that the friction between them and water molecules is far less than with other ions.

The dimensions of the ions of the metals and of the non-gaseous non-metals given by Stokes's law are compared with those calculated on the basis of the atomic volumes. The agreement is good for univalent elements, with the exception of potassium, but there

is a moderately high and approximately constant difference in the case of the bivalent metals.

T. H. P.

The Decomposition of Dielectric Liquids in the Midst of which an Arc passes. ED. URBAIN and CLAIR SCAL (*Compt. rend.*, 1919, **168**, 887—889).—An arc, started by a high-frequency spark, and continued by a current at low voltage, in passing through the tetrachloride of titanium, tin, or carbon, causes a marked decomposition, chlorine being liberated. With saturated liquid hydrocarbons, there is a liberation of acetylene, ethylene, and hydrogen, and a deposition of carbon. With pinene, the same products are obtained, and at the same time there is a marked formation of isoprene in the liquid. Ketones yield carbon monoxide and different hydrocarbons. In the case of organic dielectric liquids, the process of decomposition differs according as the liquid is maintained at 15° or at its boiling point, the decomposition being far more thorough in the latter case.

W. G.

Thermochemical Application of the Grating Theory. M. BORN (*Ber. Deut. physikal. Ges.*, 1919, **21**, 13—24).—A theoretical paper in which it is shown that the formation or decomposition of a crystalline substance must be accompanied by a heat change which is equal to the electrical energy of the grating. It is impossible to calculate this quantity with the hope of finding agreement between the experimental quantity and the calculated quantity of heat, but it is shown in the case of the alkali halogen salts, and also for the calcium halogen salts, that the order of the two quantities is the same. The formation of a crystal of sodium chloride from its elements is considered as occurring in three steps: (1) the subdivision of sodium into isolated atoms and the ionisation of these, which uses a quantity of work Z_{Na} ; (2) the subdivision of the chlorine into atoms and the ionisation of these, which absorbs work Z_{Cl} ; (3) the combination of the ions of sodium and chlorine to form the solid crystal, whereby the electrostatic crystal energy, U_{NaCl} is obtained as heat. The heat of formation is then given by $Q_{NaCl} = -Z_{Na} - Z_{Cl} + U_{NaCl}$. It is shown that $\Delta Z_{Na,K} = Z_{Na} - Z_K = U_{NaCl} - U_{KCl} - Q_{NaCl} + Q_{KCl}$ and from this $\Delta Z_{Na,K}$ is independent of the halogen. The value of U is calculated for the lithium haloids, and found to fall from the fluoride to the iodide.

J. F. S.

Thermal Conductivity of Organic Compounds. W. HERZ (*Zeitsch. physikal. Chem.*, 1919, **93**, 376—379).—A theoretical paper in which the relationship between the density (d), specific heat (c), and the thermal conductivity (k), as expressed in the equation $k = \eta \cdot c \cdot d$, is considered. It is shown that the quantity k/cd decreases in homologous series of organic compounds with increasing molecular weight and also with increasing molecular diameter. This is in keeping with the assertion of Weber (*Sitzungsber. K. Akad. Wiss. Berlin*, 1885, 809) that this quantity is

inversely proportional to the mean distance between the molecules. The heat capacity (c_d) for equal volumes of liquids and the thermal conductivity k are proportional to one another, although many exceptions to this occur. In some liquids, the heat capacity varies inversely as the thermal conductivity. J. F. S.

Equation of State for Liquids and Vapours. I. Vapour Phase of Ethyl Ether. FREDERICK G. KEYES and WILLIAM A. FELSING (*J. Amer. Chem. Soc.*, 1919, **41**, 589–619).—The authors

discuss the basal ideas of the kinetic theory in their relationship to the work of van der Waals, and they deduce an equation of state on the present-day conception of the atom. This equation has the form $p = RTx/(v - \delta) - Ax/(v - l)^2$, in which $\delta = \beta e^{-\alpha/v}$ (see *Proc. Nat. Acad. Sci.*, 1917, **3**, 323). It is shown that the strict proportionality between the pressure increment and the temperature increment at constant volume is the only trustworthy test of a system with one molecular type, and that divergence from the linear curve is due to polymerisation or change in the molecular system. The data of Ramsay and Young and other investigators for ethyl ether have been re-calculated on the above formula, and it is shown that the particular form of the mathematical function $\delta = \beta e^{-\alpha/v}$ and the cohesive pressure expression $\phi = A/(v - l)^2$ are both exact. The pt curves for ether have been measured at constant volume, and are shown to be linear within the limits of accuracy of the measurements. From the constants of these curves, the δ -equation and the ϕ -equation have been computed, and the mathematical form deduced for each shown to be exact. Amagat's data have been used to determine the equation for δ (liquid phase) on the assumption that this phase is bimolecular. The ratios of the β - and α -constants have been compared and found to be simple. For one molecule of liquid, the limiting volume correction β_2 is numerically equal to the limiting volume correction of the gas β_1 , whilst α_2 is only one half as great as α_1 . J. F. S.

Specific Heat and Latent Heat of Fusion of the Dichloro-, Chlorobromo-, Dibromo-, Bromoiodo-, and Di-iodo-benzenes. I. J. NARBUTT (*Zeitsch. Elektrochem.*, 1918, **24**, 339–342).—The

specific heat and latent heat of fusion of a number of dihalogenated benzenes have been determined. The following numerical results have been obtained: c' is the mean specific heat of the molten substance, c the mean specific heat of the solid, and g the latent heat of fusion. (1) *p*-Dichlorobenzene, $c'_2 = 0.22024 + 0.0003462(t_1 + t_2)$, c' between 99.1° and 52.9° is 0.298 ± 0.004 , $g = 29.50 \pm 0.11$ cal.; *o*-dichlorobenzene, $c = 0.185 \pm 1\%$ between -31.3° and -75.6° , $c''_2 = 0.27022 + 0.0001512(t_1 + t_2)$, $g = 21.01 \pm 0.14$ cal.; *m*-dichlorobenzene, $c = 0.186 \pm 1\%$ between -27.8° and -76.2° , $c''_2 = 0.27022 + 0.0001512(t_1 + t_2)$, $g = 20.47 \pm 0.14$ cal.; *p*-chlorobromobenzene, $c' = 0.239 \pm 0.004$ between 99.8° and 64.6° ,

$c_{12}^I = 0.17066 + 0.0002499(t_1 + t_2)$, $g = 23.42 \pm 0.09$ cal.; *o*-chlorobromobenzene, $c_{12}^{II} = 0.21497 + 0.0001174(t_1 + t_2)$, $c = 0.192 \pm 1\%$ between -15.1° and -74.8° , $g = 15.44 \pm 0.11$ cal.; *m*-chlorobromobenzene, $c' = 0.199 \pm 2\%$ at -75.8° , $c_{12}^I = 0.21224 + 0.0001174(t_1 + t_2)$, $g = 15.34 \pm 0.10$ cal.; *p*-dibromobenzene, $c_{12}^I = 0.13934 + 0.0001907(t_1 + t_2)$, $g = 20.84 \pm 0.08$ cal.; *o*-dibromobenzene, $c_{12}^{II} = 0.17994 + 0.0001070(t_1 + t_2)$, $c = 0.248 \pm 0.75\%$ between 0° and -73.2° , $g = 12.79 \pm 0.10$ cal.; *m*-dibromobenzene, $c_{12}^{II} = 0.17535 + 0.0001070(t_1 + t_2)$, $c = 0.134 \pm 1\%$, $g = 13.39 \pm 0.09$ cal.; *p*-bromiodobenzene, $c_{12}^I = 0.11627 + 0.0001576(t_1 + t_2)$, $g = 16.57 \pm 0.07$ cal.; *o*-bromiodobenzene, $c_{12}^{II} = 0.15285 + 0.0000666(t_1 + t_2)$, $c' = 0.148 \pm 2\%$ between 0° and -75.5° , $g = 12.2 \pm 2\%$; *m*-bromiodobenzene, $c_{12}^{II} = 0.15134 + 0.0000666(t_1 + t_2)$, $c = 0.143 \pm 1\%$ between -12.5° and -74.8° , $g = 10.30 \pm 0.10$ cal.; *p*-diiodobenzene, $c_{12}^I = 0.10093 + 0.0001332(t_1 + t_2)$, $g = 16.21 \pm 0.10$ cal.; *o*-diiodobenzene, $c_{12}^{II} = 0.13574 + 0.0000388(t_1 + t_2)$, $g = 10.20 \pm 0.05$ cal.; *m*-diiodobenzene, $c_{12}^I = 0.10093 + 0.0001332(t_1 + t_2)$, $c' = 0.140 \pm 0.002$ between 99.6° and 34.2° , and 0.137 ± 0.003 between 63.2° and 34.2° , $g = 11.55 \pm 0.03$ cal. The trustworthiness of the formula is tested by calculation of the mean specific heat for each set of experimental conditions, and the results in each case are well in accordance with the experimental values. J. F. S.

Specific Heat and Latent Heat of Fusion of the Dichloro-, Chlorobromo-, Dibromo-, Bromoiodo-, and Di-iodo-benzenes.

II. J. NARBUTT (*Zeitsch. Elektrochem.*, 1918, **24**, 342—354. Compare preceding abstract).—A theoretical paper in which the results recorded in the previous paper are discussed. The specific heats of the liquid isomerides of the dihalogenated benzenes are practically the same, whereas theoretically they could differ somewhat. The specific heat of very strongly supercooled dihalogenated benzenes changes according to the same rule as is followed above the freezing point. A formula is deduced for calculating the specific heat of nearly related non-associated compounds. This formula has been tested in the case of the dihalogenated benzenes. The dihalogenated benzenes, according to the rule of Longinescu (A., 1908, ii, 931), are non-associated. The critical temperature and the critical volume of several of the dihalogenated benzenes have been calculated; the following values are recorded, which are the mean of the values of the three isomerides: dichlorobenzene, T_k 689° , ϕ 2.43; chlorobromobenzene, T_k 725° , ϕ 1.95; dibromobenzene, T_k 760° , ϕ 1.65; bromoiodobenzene, T_k 809° , ϕ 1.45; chloroiodobenzene, T_k 774° , ϕ 1.66; and diiodobenzene, T_k 858° . J. F. S.

Specific Heat and Latent Heat of Fusion of the Dichloro-, Chlorobromo-, Dibromo-, Bromoiodo-, and Di-iodobenzenes. III. J. NABBUTT (*Zeitsch. Elektrochem.*, 1919, 25, 51—57. Compare preceding abstracts).—A theoretical consideration of the results recorded in part I. It is shown that the latent heat of fusion of the dihalogen benzenes decreases in general with increasing molecular weight and decreases with increasing melting point. The mean value of the quotient of the molecular latent heat, M , and the absolute melting point, T , $M/T = \phi$, has the value 13.3 for the para-series, 11.8 for the ortho-series, and 12.0 for the meta-series. The mean values do not differ very much from the individual values, consequently the latent heat of fusion can be calculated for those cases where it has not been experimentally determined. The eutectic points of the system *p*-dichlorobenzene-*p*-di-iodobenzene have been calculated and found to correspond closely with the experimental values. In some cases, the maximum work of solidification has been calculated from the data obtained for the supercooled liquids. The difference between the molecular volumes in the liquid and solid state has been calculated for several of the dihalogenated benzenes. In the case of the para-dihalogenated benzenes, the quotient of molecular latent heat of fusion and the absolute melting point is three times as large as the difference between the molecular heats at the melting point, whilst it is equal to the difference of the mean molecular heats between the melting point and the absolute zero. J. F. S.

Specific Heat and Latent Heat of Fusion of the Dichloro-, Chlorobromo-, Dibromo-, Bromoiodo-, and Di-iodobenzenes. IV. J. NABBUTT (*Zeitsch. Elektrochem.*, 1919, 25, 57—66. Compare preceding abstracts).—A mathematical consideration of the experimental results recorded in part I. It is shown that in general the solid isomerides of the dihalogenated benzenes have practically the same specific heat over the temperature range examined, but in some cases a markedly different value is obtained. The dependence of the specific heat on the temperature is greater in the solid state than in the liquid state. The specific heat changes quite regularly with temperature even in the neighbourhood of the melting point. The mean specific heat cannot be calculated by the Neumann rule to nearer than 2% even when the dependence of this factor on temperature is taken into account. The value of β_0 of the Nernst and Lindemann formula has been calculated for the various atoms, and the following values obtained: C (attached to H) 3100, C (attached to a halogen) 1400, H (attached to C) 850, Cl (attached to C) 365, Br (attached to C) 250, and I (attached to C) 100. These values are, however, not trustworthy for calculations involving extrapolation to very low temperatures. The work of expansion against the cohesive forces is the same for the gram-molecule of the solid dihalogenated benzenes. J. F. S.

Latent Heats of Fusion and their Relation to Molecular Composition. HARBORD GEORGE WAYLING (*Phil. Mag.*, 1919, [vi], 37, 495—497).—The latent heat of fusion multiplied by the molecular number (that is, the sum of the atomic numbers of the atoms in the molecule) and divided by the absolute melting point is for many compounds equal to the number of the atoms in the molecule. Thus for water $80 \times 10 \div 273 = 2.93$. For the majority of salts with water of crystallisation, the rule holds if two instead of three is allowed for the number of atoms in the water molecule. The generalisation holds for a number of inorganic salts and for formic acid and chloroform. Acetic acid, phenylacetic acid, and butyric acid all yield the same number, 5, but no simple connexion occurs for the closed-ring or aromatic compounds. F. S.

Cryoscopic Investigation of Double Salts and Complex Salts in Aqueous Solution. E. CORNEC and G. URBAIN (*Bull. Soc. chim.*, 1919, [iv], 25, 131—136).—A more detailed account of work already published (compare A., 1914, ii, 428). W. G.

The Measurement of Very Low Temperatures. XXIX. Vapour Pressures of Oxygen and Nitrogen for obtaining Fixed Points on the Temperature Scale below 0°. P. G. CATH (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, 21, 656—663).—The vapour pressures of oxygen and nitrogen have been determined at temperatures in the neighbourhood of 57° to 90° (abs.). In the case of oxygen, the results can be expressed by the equation $\log p = A/T + B + CT$ (p in atm.), with $A = -419.31$, $B = 5.2365$, $C = -0.0648$. From this equation, the normal boiling point of oxygen would be 90.13° on Kamerlingh Onnes' scale, the actually observed value being 90.14°. The nitrogen results can be expressed by a similar equation, in which $A = -334.64$, $B = 4.6969$, and $C = -0.00476$. The boiling point of nitrogen calculated from the equation is 77.31° on the same scale. Measurements of the vapour pressure of solid nitrogen give the relation $\log p = -358.73/T + 4.7769$ as holding near the triple point. This equation gives for the triple point $T = 63.25^\circ$, $p = 0.1269$ atm., or 9.64 cm. E. H. R.

Vapour Pressure and Latent Heat of Vaporisation of Silicon Hydrides and their Simple Derivatives. ROBERT WINTGEN (*Ber.*, 1919, 52, [B], 724—731. Compare Stock, Somieski, and Wintgen, A., 1918, ii, 110, 111).—A mathematical investigation of the data recorded by Stock and his co-workers on the vapour tension at various temperatures of simple silicon compounds, and the calculation of the molecular latent heat of vaporisation of the substances at any temperature. H. W.

Vapour Pressure Regularities. II. W. HERZ (*Zeitsch. Elektrochem.*, 1918, 24, 333—335).—The proportionality factor of Dühring's rule has been calculated for the substances chlorine, bromine, iodine, argon, krypton, xenon, oxygen, sulphur, nitrogen,

phosphorus, arsenic, bismuth, copper, silver, zinc, cadmium, mercury, tin, lead, and a large number of organic substances. It is shown that in all cases it exhibits an approximate constant. In the case of the non-metals, the q value increases with increasing pressure, and in every group of the periodic system with increasing atomic weight. The metals behave in the opposite way. The q value for compounds in most cases exhibits a tendency to increase with increasing molecular weight in each group of the periodic system and in each homologous series of organic substances.

J. F. S.

Molecular Theory of the Vapour Pressure of Solid Substances and its Significance in the Calculation of Chemical Constants. OTTO STERN (*Zeitsch. Elektrochem.*, 1919, 25, 66—80).—A mathematical paper in which a theory of the vapour pressure of solid substances is developed on the basis of the following four hypotheses: (i) The attractive forces between atoms in the gaseous phase may be neglected on account of the relatively great distance between the atoms. (ii) The atoms exercise attractive forces on one another in the solid phase, and these forces are in equilibrium about the centres of gravity of the atoms. In the case of crystals, these forces are arranged orderly in the crystal grating. (iii) The atomic forces operate so that when an atom moves from its position of equilibrium, an opposing force is set up which tends to bring it back into the position of equilibrium. The magnitude of this force is proportional to the amount of movement of the displaced atom. (iv) To move an atom from its position of equilibrium, a definite finite amount of work, ϕ_0 , is necessary, so that $N\phi_0 = \lambda_0$ is the heat of sublimation at the absolute zero, on the assumption that at this point all atoms are in their equilibrium positions. Complicated formulæ are developed on these assumptions, and these take account of the different frequencies of the atoms. From these formulæ others are developed for calculating the chemical constants.

J. F. S.

Vapour Pressure of Acetone-Chloroform Mixtures. ALFRED SCHULZE (*Zeitsch. physikal. Chem.*, 1919, 93, 368—375).

—The vapour pressure of various mixtures of acetone and chloroform has been determined at 30°, 70°, and 90°, and composition-pressure curves constructed for the three temperatures. The curves indicate that acetone-chloroform mixtures contain an equimolecular compound of the two constituents in a dissociated condition, which with increasing temperature apparently becomes less. At 30°, a distinct association of acetone is noticeable. By the aid of the law of mass action, the vapour pressure of the various mixtures was calculated, and the results shown to be in good agreement with the experimental values.

J. F. S.

Explosion, Implosion, and Bursting. WALTER BRIEGER and HANS SCHIMANK (*Zeitsch. Elektrochem.*, 1918, 24, 354—356. Compare A., 1917, ii, 462).—A discussion on the exact definition of

the term explosion. An explosion is defined as the sudden development of a gaseous volume, an implosion as the sudden disappearance of a gaseous volume. Bursting may be occasioned by either process or by inequalities of pressure or strain. J. F. S.

Calculation of the Density of some Elements at the Absolute Zero. W. HERZ (*Zeitsch. anorg. Chem.*, 1919, 105, 171—174).—The densities and atomic volumes of a number of elements at absolute zero have been calculated, making use of Lorenz's relation between the volume at absolute zero and that at the critical point, boiling point, and melting point (A., 1916, ii, 312). These relationships are given by the equations $d_0 = 1.41d_c = 3.75d = 1.21d_c = d(0.77 + 0.64T/T_c)$, in which d is the density, T is the absolute temperature, and the suffixes c , s , k , and e represent, respectively, absolute zero, boiling, critical, and melting points. The values of d_0 calculated from the different equations do not always show very good agreement; in the case of mercury, for instance, d_0 varies between 14.23 and 17.41. It is claimed, however, that in most cases a very fair approximation to the true value is obtained. Sodium (1.083) has a greater zero density than potassium (1.004), but in all other cases the density increases with the atomic weight. E. H. R.

Physical and Chemical Theories [of the Action of Toxins, Dyes, etc.]. I. TRAUBE (*Chem. Zeit.*, 1919, 43, 129—130).—Polemical. A continuation of the controversy with Karrer (Traube, A., 1912, ii, 740; Karrer, A., 1918, ii, 431).

Measurement of the Thickness of Film formed on Glass and Sand. EARL PETTIJOHN (*J. Amer. Chem. Soc.*, 1919, 41, 477—486).—A method is described by which the thickness of a film of liquid, capable of forming on the surface of sand and glass beads without free liquid being present, may be measured. The method consists in placing a known weight of sand (200 grams) in a dry, conical flask and adding the liquid drop by drop from a burette with repeated shaking after each addition until particles of the sand adhere to the walls of the flask. The adherence to the walls is taken to indicate the presence of free liquid. The surface of the sand or beads is then determined, and the thickness of the film calculated. These experiments were carried out with water, nitrobenzene, aniline, dimethylaniline, iodobenzene, toluene, turpentine, and pyridine, and with sands and beads of varying diameter. The results show that there is no chemical combination between the liquid and the solid. The thickness of the film is independent of the liquid used and of the size of the solid particles. J. F. S.

Formulae concerning Surface Tension. ARTHUR C. LUNN (*J. Amer. Chem. Soc.*, 1919, 41, 620—621).—A theoretical discussion on the mathematical processes involved in the deduction of the formulae used for calculating surface tension. J. F. S.

Determination of Surface Tension (Free Surface Energy), and the Weight of Falling Drops: Surface Tension of Water and Benzene by the Capillary Height Method.

WILLIAM D. HARRIS and F. E. BROWN (*J. Amer. Chem. Soc.*, 1919, **41**, 499–524).—The two methods in general use for the determination of surface tension are considered, the errors attached to each method are indicated, and a series of determinations of the surface tension of water and benzene are recorded. The theory of the capillary rise method is simple, but the technique is difficult, and its use in some cases causes errors as high as 30%, due to its inapplicability to certain classes of substances. The drop-weight method is applicable to a wide range of liquids, and the technique is not difficult; but the theory of this method has not been completely worked out, so that many of its published results are inaccurate, although the experimental data are accurate; this is due to the use of an inaccurate theory. The relation of the experimental results of the drop-weight method to those of the capillary rise method has been determined by using liquids which give accurate results by both methods, and this relationship has been plotted in such a way as to show the relation between surface tension and the form of the drop which falls from a circular tip. The surface tension and the capillary constant of water and benzene at 20°, each against air saturated with its own vapour, have been determined by the capillary rise method. The values obtained are: for water, $\gamma = 72.800$ dynes per cm., $a^2 = 14.897$ mm.; for benzene, $\gamma = 28.80$ dynes per cm., $a^2 = 6.713$ mm. In this determination, the capillary tubes were steamed out with the vapour of the liquid before use. In the case of water, this increased the value of γ by about 0.1 dyne. Water, benzene, carbon tetrachloride, and ethylene dibromide were dropped from a large number of glass and metal tips of radii varying from 0.09946 cm. to 1.0028 cm., and the weights of the falling drops determined. From the data, r/a and $f(r/a)$, of the Lohmstein equation,

$$Mg = 2\pi r \gamma f(r/a),$$

were calculated for values of r/a between 0.25 and 2.60. The value of $f(r/a)$ is not constant, but varies from 0.7256 to 0.5352 in this range, whilst when r/a falls to 0.025, $f(r/a)$ rises to 0.924. It is assumed that in conjunction with other necessary conditions, r/a really determines the shape of the hanging drop, and that it is the shape of the drop which determines the fraction of the drop which falls. This shape may also be determined by the ratio of r to the cube root of the volume of the falling drop. Thus a new equation, similar to that of Lohmstein, was derived,

$$Mg = 2\pi r \gamma \psi(r/v^{1/3}).$$

This is more easily applied to the determination of surface tension than Lohmstein's equation, since all the factors except γ are obtained by direct experiment or from a table of values, whilst the a of Lohmstein's equation cannot be obtained from the direct results of the drop-weight measurements, but must be calculated by methods of approximation.

J. F. S.

Osmotic-kinetic Theory of Dilute Solutions. G. JÄGER (*Zeitsch. physikal. Chem.*, 1919, **93**, 275—311).—A theoretical paper in which the relationship between pressure and volume of a highly compressed gas is deduced. It is shown both as a first approximation and also strictly that that portion of the pressure of a highly compressed gas occasioned by the arrangement of the molecules on a surface can be calculated as though no collisions between the molecules occurred. To this portion of the pressure there is to be added that occasioned by the collisions of the molecules. The sum of the two gives the pressure exerted on the walls of the containing vessel. Calculations show that for a solution an osmotic pressure is obtained which is the same as the value which would be obtained if the dissolved substance alone were present in the vessel. It is also shown that a dilute solution must have the same internal pressure as the pure solvent. The equations for the elevation of the boiling point and the lowering of the freezing point are developed from the vapour-pressure lowering. It is also shown that the Nernst theorem can be obtained from kinetic considerations, and that the relationship of the concentrations of a non-electrolyte in two sparingly soluble solvents is independent of the quantity of dissolved substance. J. F. S.

Rapid Determination of Solubility. T. J. WARD (*Analyst*, 1919, **44**, 137).—About 3 c.c. of the solvent are heated in a test-tube placed in a beaker of water about 10° to 20° higher than the temperature at which the solubility is to be determined, and small quantities of the substance are added, with constant shaking, until some remains undissolved. The test-tube is then immersed in water at the desired temperature for ten minutes, with occasional shaking, after which a thimble of filter-paper is pushed into the tube so that the liquid can filter inwardly. A definite volume of the filtrate is withdrawn by means of a pipette, weighed in a covered vessel, and evaporated, and the residue dried and weighed. C. A. M.

Coagulation of Metal Sulphide Hydrosols. I. Influence of Distance between the Particles of a Sol on its Stability. Anomalous Protective Action of Dissolved Hydrogen Sulphide. JANENDRA NATH MUKHERJEE and NAGENDRA NATH SEN (*T.*, 1919, **115**, 461—472).

The Chemical Equilibrium between Lead Sulphide and the Products of the Roasting Process. RUDOLF SCHENCK and AGNES ALBERS (*Zeitsch. anorg. Chem.*, 1919, **105**, 145—166).—The three-component system lead-sulphur-oxygen gives rise to seven solid phases, Pb, PbO, PbS, PbSO₄, PbSO₃, PbO, PbSO₄.2PbO, PbSO₄.3PbO, besides the gaseous phase SO₂. There are thirteen possible univariant systems, each consisting of three solid phases in equilibrium with the gaseous phase, and these

thirteen systems fall into three groups. In group I (4 systems), lead sulphide is in equilibrium with two oxygen-containing phases; in group II (5 systems), lead sulphide and metallic lead are in equilibrium with one oxygen-containing phase; and in group III (4 systems), metallic lead with two oxygen-containing phases. The vapour-tension curves for the systems of groups I and II have been investigated at temperatures between 500° and 820°. Earlier measurements of the vapour tensions of some of these systems were made by Schenck (A., 1907, ii, 546, 619) and Reinders (A., 1915, ii, 47), but their results were to some extent vitiated through the use of silica vessels, which were attacked by the reaction mixtures. This difficulty has been overcome by the use of calcium phosphate for the containers. The pressure-temperature diagram for the nine systems investigated is given. The most stable phases are those of group II, in which both lead and lead sulphide are present as solid phases, these systems being in equilibrium with a lower pressure of sulphur dioxide than those of group I. The vapour phase always contains lead sulphide. It follows that in the systems of group III, in which lead sulphide is not present as a solid phase, the vapour must be unsaturated with respect to lead sulphide. A complete equilibrium diagram, including the systems of group III, must therefore be in three dimensions, the third co-ordinate representing the vapour pressure of lead sulphide. It was found impossible to realise experimentally the conditions of existence of the systems of group III, as they are apparently very unstable.

The vapour pressure of lead sulphide between 850° and 1000° was measured, and was found to increase from 2 mm. to 17 mm. between these temperatures. Lead sulphide distils readily in a vacuum at 900°.

E. H. R.

The Action of Salts. K. SPIRO (*Biochem. Zeitsch.*, 1919, 93, 384—394).—Many ions may have an influence on quite simple chemical reactions in which they are apparently not directly concerned. The influence of the ions may be arranged in order of magnitude, resembling the Hofmeister series.

The reactions studied included the oxidation of potassium iodide by atmospheric oxygen and hydrogen peroxide, the oxidation of indigo, the guaiacum reaction, the reducing action of hydrogen peroxide on ferric chloride and potassium ferricyanide, the oxidation of ammoniacal cuprous and silver oxides by dextrose, the indophenol reaction, and the action of catalase. The series of ions are not identical in every case. The presence of magnesium may in certain cases exert a more favourable action on oxidation processes than that of sodium, but examples of the reverse condition occur. Certain examples of the influence of foreign ions may be considered to be analogous to co-enzyme actions. It is apparent, however, that the lyotropic series may apply for simple chemical reactions as much as for physico-chemical reactions, such as imbibition or emulsification.

J. C. D.

Catalytic Action of Hydrogen Ions in Hydrolyses. RUD. WEGSCHEIDER (*Ber.*, 1919, **52**, 235—236).—The failure of hydrogen ions to catalyse the hydrolysis of β -lactones is not the first example of abnormality in hydron catalysis (see Johannsson and Sebelius, A., 1918, ii, 223). Sulphonic esters are also known to be uninfluenced in this way, although the hydrolysis of alkyl hydrogen sulphates is catalysed by hydrions. J. C. W.

Temperature-coefficient of Catalysed and Non-catalysed Reactions. N. R. DHAR (*Ann. Chim.*, 1919, [ix], **11**, 130—223).—A more detailed account of work already published (T., 1917, **111**, 707). W. G.

Conception of Chemical Elements and Atomic Weight Tables. RUD. WEGSCHEIDER (*Zeitsch. physikal. Chem.*, 1919, **93**, 380—381).—Polemical against the definition of the term element put forward by Paneth (compare A., 1916, ii, 240; 1918, ii, 304). J. F. S.

Valency Theory. A. E. LACOMBLÉ (*Zeitsch. physikal. Chem.*, 1919, **93**, 257—274).—A theoretical paper in which, on the basis of Kossel's (A., 1916, ii, 243) conception of the atom, the author develops a theory of valency. As hypothesis, the following assumptions are made: (i) The electrons situated on the outside ring are stationary. (ii) A sphere is supposed to surround the atom in such a way that its centre lies at the centre of gravity of the atom, and only the outermost sheath falls outside the atom. The field of forces of the nucleus is regarded as that of a sphere of stated size having on its surface an irreplaceable positive charge of dimensions equal to, but opposite in sign to, the sum of the electrons on the outermost sheath. (iii) Chemical combination is regarded as the replacement of the curved lines of force between atoms and their electrons by shorter and straight lines of force. On the basis of these assumptions, the nature of the compounds which are formed between various elements is deduced. For example, it follows that the stability of the oxygen derivatives of the halogens increases with increasing atomic weight of the halogen. The halogen derivatives of the elements of group 6 increase in stability with increasing atomic weight of the element of the sixth group. Many other cases are developed. The nature of the bonds in the formation of molecules of elements is considered. This is divided into three types, which differ in the density of the lines of force on the atoms. The paper concludes with a description of the nature of the bonds of organic compounds. J. F. S.

The Mythical Basil Valentine. W. HOMMEL (*Zeitsch. angew. Chem.*, 1919, **32**, i, 73—76).—Although the existence of the alleged fifteenth-century monk, Basil Valentine, was doubted by Gmelin (1797), and by Kopp in his later work (1886), he is still, in many quarters, regarded as the last of the alchemists.

Anachronisms in the supposed writings of Basil Valentine prove that these could not have been written as early as 1460. All the evidence indicates that the name was a pseudonym for Johann Thölde, who, in 1603—1604, first published the writings of "Basil Valentine." The survival of the myth down to the present day is largely attributable to the account in Kopp's "Geschichte der Chemie" (1843), whilst Kopp's later conclusion on the subject has been overlooked.

C. A. M.

Simple Efficient Vacuum Pump for Laboratories. MAX VOLMER (*Ber.*, 1919, 52, [B], 804—809).—The pump is constructed on principles similar to those of Langmuir (*Phys. Rev.*, 1916, 8, 48) and Kraus (*A.*, 1917, ii, 567), from which it differs considerably in detail. The mercury is boiled in a glass vessel, and the vapour, passing through a narrow tube into the cooling chamber, carries with it the air from the vessel to be exhausted and passes it into the fore-vacuum of a water pump; the condensed mercury flows back by a side-tube to the bottom of the boiler, direct connexion between the fore- and main-vacua being prevented by a bent tube, in which mercury collects. The apparatus is figured in the original.

The average efficiency of the pump is such that a litre flask can be exhausted from 15 mm. to $<1/100$ mm. in five minutes, but differs somewhat with different individuals, as it depends on small factors which cannot invariably be reproduced. It is easily manipulated and cleaned. Vapours are removed as readily as gases, and it is not sensitive to moderate amounts of halogens. Its use is recommended for drying substances and for distillation under greatly diminished pressure. By the aid of the pump, more complete desiccation can be effected in thirty minutes than by exposure to alkali hydroxide at 10 mm. during twenty-four hours.

H. W.

Gas Washing Flask, especially for Use in the Estimation of Sulphur Dioxide in Flue Gases. H. SCHILLING (*Chem. Zeit.*, 1919, 43, 167).—The central inlet tube and the exit tube leading from the stopper of the flask are connected by means of a short length of tube provided with a tap. By means of the latter, when suitably turned, the gases may be directed through the solution contained in the flask or passed directly through the connecting tube and tap without entering the flask.

W. P. S.

Very Simple Form of Electrolytic Current Interrupter for Demonstration Purposes. KARL BRUNNER (*Ber.*, 1919, 52, [B], 629—630).—The apparatus consists of a glass trough with parallel sides, holding about 2 litres; on the one side, a lead plate, 9 × 13 cm., is suspended in 8% sulphuric acid. A board, laid on the top of the vessel, serves as adjustable support for a glass tube of 16 mm. diameter, at the bottom of which a hole, 3—4 mm. in diameter, is blown. The hole is partly closed by a pointed glass

rod, 50 mm. long and weighing 0.9 gram, which forms a valve opening in the upward direction. A strip of lead, 10 mm. wide, extends to the bottom of the tube. The apparatus is readily constructed from available material. In comparison with the Wehnelt interrupter, it gives a rather shorter spark, but is more trustworthy and less noisy in action.

H. W.

Lecture Experiment [Combustion of Phosphorus]. KARL BRUNNER (*Ber.*, 1919, 52, [B], 631—632).—The phenomena attending the combustion of phosphorus are conveniently and safely demonstrated in the following manner. The apparatus consists of two doubly tubulated glass vessels holding about a litre, which are connected by a short length of slightly bent quartz tube; the other tubulures carry a mercury manometer and a stopcock respectively. About 0.5 gram of yellow phosphorus is placed in the quartz tube, and the complete apparatus is accurately counterpoised. The phosphorus is ignited by gently warming the tube, and slow combustion is maintained by occasional gentle warming of the glass vessels. When combustion is complete, the apparatus is left to itself until the manometer indicates a deficiency in internal pressure. The weight is found to be unaltered. The stopcock is now opened, when a distinct increase in weight is caused by the inrushing air.

H. W.

Preparation of Phosphorus Trioxide as a Lecture Experiment. HEINRICH BILTZ and ANNA GROSS (*Ber.*, 1919, 52, [B], 762—768).—The apparatus consists of a combustion tube, 30 cm. long and 1.8—2.0 cm. internal diameter, which is drawn out to a point and turned upwards at one end. This is connected with a filter tube, 25 cm. in length and of the same diameter as the first tube, which contains a loose plug of cotton wool and a layer of 6 cm. of tightly compressed cotton-wool balls. During the experiment, the tube (which is preferably made of brass) is heated at 50—60° by a small flame. A condensation tube, 75 cm. long and 2 cm. wide, is connected with the filter tube and, through a wash-bottle containing sulphuric acid, to a filter pump. About 10 grams of phosphorus are placed in the combustion tube, the filter tube is warmed, and the experiment started by gently warming the phosphorus until it is just ignited; after about two minutes, when the tube has become warmed, the speed of the air stream is considerably increased. After five to ten minutes, phosphorus trioxide begins to appear in the condensation tube, which is cooled, if necessary, by a cloth dipped in ice-water. The experiment must be stopped before the phosphorus is completely burnt; if not, oxygen gets access to the phosphorus trioxide and causes oxidation. The crystalline nature and low m. p. of the trioxide are readily demonstrated; the oxidisability is shown by opening the tube in the dark, when a luminescence is shown which develops into active combustion when the tube is warmed or by dissolving the substance

in carbon disulphide, so as to obtain a dilute solution, which is then poured on to filter paper.

The authors are led to the conclusion that phosphorus trioxide is always the primary product of the combustion of phosphorus, and that formation of the pentoxide is a subsequent reaction. They therefore recommend the use of a rapid air current, since this ensures on the one hand a rapid combustion, and consequent complete removal of oxygen from the residual gases, and on the other a rapid withdrawal and cooling of the phosphorus trioxide, which is otherwise readily decomposed into phosphorus pentoxide and red products.

The yield of phosphorus trioxide is only moderate, and the addition of indifferent gases, either before or behind the zone of combustion, does not effect sufficient improvement to justify the complication involved.

H. W.

Inorganic Chemistry.

Hypochlorous Acid and Chlorine Monoxide. STEFAN GOLDSCHMIDT (*Ber.*, 1919, 52, [B], 753—761).—Aqueous solutions of hypochlorous acid containing 25% of the acid are readily obtained by distilling a mixture of chlorine hydrate and yellow mercuric oxide in a good vacuum; attempts to prepare the more concentrated solution or the anhydrous acid by distillation of this acid in a moderate vacuum, and condensation of the distillate in receivers maintained at 0°, -20°, and -80°, led to an unexpected result, since in the first two vessels aqueous hypochlorous acid (25%) was collected, whilst in the third vessel pure chlorine monoxide was condensed (the pure monoxide has b. p. +3.8°/766 mm. and can only be preserved without decomposition for any length of time at -80°). It therefore appeared that the aqueous acid

contains two systems in equilibrium: (1) $\text{HClO} \rightleftharpoons \overset{+}{\text{H}} + \overset{-}{\text{OCl}}$, and (2) $\text{HClO} \rightleftharpoons \text{Cl}_2\text{O} + \text{H}_2\text{O}$. The latter system has been investigated by agitating aqueous hypochlorous acid solutions of different concentration with an equal volume of carbon tetrachloride at 0°, separating the solutions, and estimating the active chlorine in each by titration with sodium thiosulphate after treatment with acidified potassium iodide solution. The equilibrium lies greatly in favour of the hypochlorous acid, so that an approximately *N*/5-solution contains 0.02% of the anhydride.

The well-known greater oxidising power of hypochlorites in acid than in alkaline solution is probably due to chlorine monoxide contained in the former solutions.

H. W.

Preparation of Sulphuryl Chloride. A. BOAKE ROBERTS and Co., LTD., and THOMAS HAROLD DURRANS (Brit. Pat., 124542).—Sulphur dioxide and chlorine, in equal volumes, are passed either together or alternately, and either continuously or intermittently, into a vessel containing a suitable catalyst. The temperature must be kept sufficiently low to prevent the catalyst and the sulphuryl chloride formed from volatilising, and sufficiently high to prevent the catalyst from solidifying. The sulphuryl chloride may be isolated by distillation or other suitable means.

The following classes of substance are effective as catalysts, and do not require the aid of light or pressure, the most suitable members of each class being placed within brackets: terpene hydrocarbons (pinene and limonene); esters which are compounds of saturated acids or of monohydroxyphenols with monobasic aliphatic acids containing carbon, hydrogen, and oxygen only (methyl acetate, isoamyl formate, ethyl butyrate, phenyl acetate, phenyl-ethyl acetate, glyceryl triacetate, oils which are esters of glycerol, and also triphenyl phosphate and tritolyl phosphate); ethers which are the mixed or simple saturated aliphatic ethers (ethyl ether, isobutyl ether, benzyl ether, tolyl ether), and the terpene ether, cineole (eucalyptol); the saturated monohydroxyphenols which contain only one benzene ring. The ethers, phenols, and esters are limited to those which contain carbon, hydrogen, and oxygen only, and no substituting groups except those containing only carbon and hydrogen. [See also *J. Soc. Chem. Ind.*, 1919, June.]

H. W.

Colloidal Selenium. JULIUS MEYER (*Zeitsch. Elektrochem.*, 1919, 25, 80—82).—Colloidal selenium may be obtained by the action of dilute sulphuric acid on sodium selenosulphate according to the equation $\text{Na}_2\text{SeSO}_3 + \text{H}_2\text{SO}_4 = \text{Se} + \text{SO}_2 + \text{H}_2\text{O} + \text{Na}_2\text{SO}_4$. A small quantity of sodium sulphite is dissolved in 5 c.c. of distilled water and boiled with an equal quantity of selenium for about half a minute, the solution is filtered, and about 1 c.c. of the filtrate diluted with a litre of water, treated with four to five drops of dilute sulphuric acid, and stirred. The solution becomes at once orange-yellow to dark red in colour, depending on the concentration. Filtration through a Zsigmondy membrane gives a clear, colourless sol. The sols are very stable and not at all sensitive to moderate concentrations of acids. The particles are positively charged, and thus differ from the colloidal selenium produced by the solution of selenium in hydrazine hydrate, which is negatively charged. A comparison of the two forms of colloidal selenium is given in the paper, and the suitability of the new form for lecture experiments is demonstrated.

J. F. S.

The Decomposition of Nitrous Acid. JOSEPH KNOX and DOUGLAS M. REID (*J. Soc. Chem. Ind.*, 1919, 38, 105—108x).—The nitrous acid solutions for these experiments were prepared by mixing solutions of nitric acid and sodium nitrite of known

strengths. The rate of decomposition of the nitrous acid was found to be profoundly influenced by the conditions. It is greatly accelerated when the amount of surface exposed to the action of air is increased, for example, by shaking in presence of excess of air. The excess of air is effective through removing by oxidation the nitric oxide produced in the reversible reaction, $3\text{HNO}_2 \rightleftharpoons \text{HNO}_3 + 2\text{NO} + \text{H}_2\text{O}$, thus allowing the balanced reaction to proceed in the direction from left to right. The nitric oxide can also be removed from the solution by the passage of a current of carbon dioxide, the decomposition being accelerated almost as much as by a current of air. The influence of temperature on the rate of decomposition with, and without, excess of air was studied up to 50°C , and the rate was found to increase rapidly with the temperature. Free nitric acid, if present, accelerates the initial rate of decomposition of the nitrous acid, but appears to have a retarding influence in the later stages. The several series of experiments are illustrated by curves.

E. H. R.

Densities of Mixtures of Sulphuric and Nitric Acids. PAUL PASCAL and M. GARNIER (*Bull. Soc. chim.*, 1919, [iv], 25, 142–145).

—Tables are given showing the results of determinations of the density of sulphuric and nitric acids at different concentrations, and of mixtures of these acids in varying proportions and with varying proportions of water added. It is shown that, in the zone of mixtures used for nitrating cotton, the density is almost entirely a function of the water content.

W. G.

Bayer's Strain Theory and the Structure of the Diamond.

ERNST MOHR (*J. pr. Chem.*, 1918, [ii], 98, 315–353).—A theoretical paper in which the stability of the cyclohexane ring is first considered; it is shown that the number of known isomerides is readily explicable by means of Lachse's model (in which the carbon atoms do not lie in one plane) if, at the same time, a free or only partly hindered rotation is assumed. The ideas are extended to more complex rings, but the data are too restricted to allow any very general conclusions to be drawn.

It is further shown that atom model systems can be constructed by the direct or oblique superposition of cyclohexane ring layers in the centre of which all valencies are saturated without strain and in which free valencies exist only at the surface. The diamond space lattice described by Bragg is then found to be identical with the obliquely formed carbon atom system so derived.

The existence of carbon rings which contain more than six carbon atoms and which are free from strain is also considered, but the author is led to the conclusion that the strain in such systems cannot at present be predicted with any certainty, and is probably complicated by other factors.

H. W.

Attempted Synthesis of Carbonyl Sulphide by means of the Electric Spark. F. GONZÁLEZ and E. MOLES (*Anal. Fis. Quím.*, 1919, 17, 55–59).—The assertion of Chevrier (*Compt.*

rend., 1869, 69, 136) that sulphur vapour and carbon monoxide combine easily under the action of the electric spark to form carbonyl sulphide was tested by the authors. Pure dry carbon monoxide was passed in a sealed apparatus over the surface of sulphur heated at 110° and 260°, and there subjected to sparking. The gaseous products were cooled in various freezing mixtures, finally in liquid air. No trace of carbonyl sulphide was observed. An experiment under reduced pressure also yielded a negative result.

W. S. M.

Thermal Decomposition of Carbonyl Sulphide. ALFRED STOCK and PAUL SEELIG (*Ber.*, 1919, 52, [B], 681—694).—The thermal decomposition of carbonyl sulphide leads to the formation of carbon monoxide and sulphur on the one hand and to carbon dioxide and carbon disulphide on the other; assuming that carbon oxysulphide is immediately concerned with each equilibrium, the reactions may be written $2\text{COS} \rightleftharpoons 2\text{CO} + \text{S}_2$ and $2\text{COS} \rightleftharpoons \text{CO}_2 + \text{CS}_2$. Attempts have now been made to determine the equilibrium at 800° and 950° respectively. For this purpose, a current of carbonyl sulphide is sent through an electrically heated quartz tube packed with quartz splinters and provided with a quartz rod to prevent backward diffusion of gas; the end of the quartz tube is drawn out to a capillary connected as closely to the furnace as possible with a quartz U-tube, which is immersed in a paraffin bath maintained at 130°, and serves to retain the sulphur; the gases evolved are collected over mercury and analysed by the authors' method (this vol., ii, 245). The effect of the rate of passage of gas (time of heating) and rapidity of cooling (length of capillary) has been investigated, from which it appears that the values observed approximate closely to the true equilibria values.

At 800°, the reaction $2\text{COS} \rightleftharpoons \text{CO}_2 + \text{CS}_2$ appears to proceed slowly in either direction, whilst the action $2\text{COS} \rightleftharpoons 2\text{CO} + \text{S}_2$ is very rapid. The fact that the carbon monoxide degree of dissociation is independent of the amounts of carbon dioxide and carbon disulphide present shows that carbon monoxide and sulphur (at any rate for the greater part) are primary products of the decomposition of carbonyl sulphide, and not formed secondarily from carbon dioxide and carbon disulphide. The CO_2 degree of dissociation is about 48·5%, the CO degree about 45·5%, so that, at 800° and atmospheric pressure, the carbonyl sulphide is decomposed to the extent of about 64%. At 950°, the corresponding figures are 43% for the CO_2 degree of dissociation, at least 71% for the CO degree, and at least 76% for the dissociation of carbon oxysulphide.

[With W. OTTMANN.]—Preliminary experiments on the action of heat on mixtures of carbon dioxide and disulphide on the one hand and of carbon monoxide and sulphur on the other show that the same products are formed as when carbonyl sulphide is heated, and that a true case of equilibrium is presented. Similarly, the combustion of carbon disulphide with an insufficiency of oxygen

or of oxygen in carbon disulphide vapour yields a mixture of unchanged carbon disulphide, carbon dioxide, sulphur dioxide, carbonyl sulphide, and carbon monoxide.

The literature of the subject is also critically reviewed.

H. W.

Stabilisation of Dilute Sodium Hypochlorite Solutions (Dakin's Solution). GLENN E. CULLEN and ROGER S. HUBBARD (*J. Biol. Chem.*, 1919, **37**, 511—517).—The regulation of the alkalinity of Dakin's solution may be efficiently carried out either by means of buffer salts or by small amounts of alkali. 0.5% Sodium hypochlorite, prepared by electrolysis of sodium chloride, may be stabilised for use by the addition of 0.5% borax, of 0.5 to 1.0% of sodium carbonate mixtures of p_H 10 to 9.5, or by the addition of 0.2 gram of sodium hydroxide per litre. J. C. D.

Electrolytic Preparation of Dilute Sodium Hypochlorite Solutions (Dakin's Solution). GLENN E. CULLEN and ROGER S. HUBBARD (*J. Biol. Chem.*, 1919, **37**, 519—523).—The influence of temperature on this process was investigated. The optimum point of the curve representing the production of hypochlorite may be raised by raising the initial temperature of the brine. Increase of salt concentration lessens the internal resistance of the cell, and consequently increases the production of sodium hypochlorite per unit of time. [See, further, *J. Soc. Chem. Ind.*, 1919, June.] J. C. D.

The Stability of Javel Extracts. H. FONZES-DIACON (*Bull. Soc. chim.*, 1919, [iv], **25**, 206—208).—Javel extracts, containing 5 grams of active chlorine per 100 c.c., lose very little of their activity when exposed to light in deep yellow bottles, even after four months. In colourless bottles, the loss is very marked, however, Javel extracts of various strengths tending towards a common limit of about 1 gram of active chlorine per 100 c.c. W. G.

Chemical Decomposition and Electrolytic Formation of Sodium Hyposulphite. K. JELLINEK and E. JELLINEK (*Zeitsch. physikal. Chem.*, 1919, **93**, 325—367).—The decomposition of sodium hyposulphite has been studied in aqueous solution and in solutions of sodium hydrogen sulphite of various concentrations at the temperatures 0°, 10°, 20°, and 30°. The reaction follows the scheme $2\text{Na}_2\text{S}_2\text{O}_4 = \text{Na}_2\text{S}_2\text{O}_5 + \text{Na}_2\text{S}_2\text{O}_3$; $\text{Na}_2\text{S}_2\text{O}_5 + \text{H}_2\text{O} = 2\text{NaHSO}_3$. The reaction is bimolecular, and the constants have been obtained for the various temperatures. The dependence of the reaction constant on temperature and on the hydrogen sulphite concentration is given by the equation $\log k = A + Bt$, in which A and B are constants. At constant temperature, the reaction constant is proportional to the square of the hydrogen sulphite concentration. The electrolysis of sodium hyposulphite has been investigated, particularly in connexion with the factors which

govern the hyposulphite formation. The electrolysis was carried out with electrodes of various metals, and variable quantities of sulphur dioxide were led into the solution. The concentration of sodium thiosulphate and the amount of hydrogen liberated were measured, and the dependence of these on the time of electrolysis determined. Solutions containing 7–8% of hyposulphite could be obtained. The processes which influenced the current yield were quantitatively explained, and the conditions for obtaining higher yields of hyposulphite indicated.

J. F. S.

Cryoscopic Study of Couples. Cadmium Iodide-Alkali Iodide. E. CORNEC and G. URBAIN (*Bull. Soc. chim.*, 1919, [iv], 25, 137–142).—For the most part a more detailed account of work already published (compare A., 1914, ii, 428). A cryoscopic study of the couple cadmium iodide–hydrogen iodide in aqueous solution reveals the existence in aqueous solution of the acid salt, $\text{CdI}_2 \cdot 2\text{HI}$.

W. G.

The Preparation of Cadmium Suboxide. HENRY GEORGE DENHAM (T., 1919, 115, 556–559).

New Preparation of a very Dissociable Calomel. PAUL DURET (*Ann. Inst. Pasteur*, 1919, 33, 174–176).—Calomel may be prepared in a light, voluminous form having a high degree of purity by the following process. A solution containing 6 grams of sodium hydrogen carbonate and 10 grams of dextrose in 80 c.c. of water is added to a solution containing 7.5 grams of crystalline magnesium chloride in 20 c.c. of water, and this mixture is added to a solution containing 11.5 grams of mercuric chloride and ten drops of hydrochloric acid in 100 c.c. of water in a flask. When the reaction has ceased, the mixture is heated on a water-bath until all the carbon dioxide is evolved. The finely divided precipitate of mercurous chloride is then collected and washed with water. In this form it possesses greater germicidal powers than the ordinary preparations when used in prophylactic ointments or anti-syphilitic injections.

W. G.

Regeneration of Nessler's Solution. D. PULLMAN (*Analyst*, 1919, 44, 124–125).—Residues from the estimation of ammonia by Nessler's method are neutralised and treated with a solution of a soluble mercuric salt in amount equivalent to the iodine present. This precipitates mercuric iodide, which may be washed, dried, and used for the preparation of a modified Nessler's solution. This is made by adding metallic zinc to mercuric iodide suspended in hot water, when the reaction, $\text{Zn} + 2\text{HgI}_2 = \text{ZnHgI}_4 + \text{Hg}$, takes place. The zinc mercuric iodide remains in solution, and, after filtration from the mercury, is treated with sodium hydroxide in sufficient quantity to produce the reagent. Experiments have shown that Nessler's reagent thus prepared can replace the ordinary solution containing potassium mercuric iodide. [See also *J. Soc. Chem. Ind.*, 1919, June.]

C. A. M.

Mercuric Sulphoxychloride. SIR PRAFULLA CHANDRA RAY and PRAFULLA KUMAR SEN (T., 1919, 115, 552-556).

Manganates and Permanganates. I. Course of the Reaction between Manganese Dioxide, Potassium Hydroxide, and Oxygen, and the Manufacture of Potassium Manganate. H. I. SCHLESINGER, R. D. MULLINIX, and S. POPOFF (*J. Ind. Eng. Chem.*, 1919, 11, 317-323).—When manganese dioxide is heated with potassium hydroxide in a current of air, complete oxidation is frequently attained only by re-moistening and re-heating the mixture. The yield of potassium manganate varies with the proportion of potassium hydroxide present; at about 300°, practically all the manganese dioxide is converted into manganate when two molecules of potassium hydroxide are used for each molecule of manganese dioxide. Manganate-manganates are not formed under these conditions, but larger amounts of potassium hydroxide cause the manganate to decompose into manganate-manganate (compare Sackur, A., 1911, ii, 400). The yield of manganate is lowered when sodium hydroxide is used in place of potassium hydroxide. It is important that the manganese ores used should be powdered as finely as possible. [See, further, *J. Soc. Chem. Ind.*, 1919, 321A.] W. P. S.

Complex Compounds of Tervalent Iron with Hypophosphorous Acid. R. F. WEINLAND and WALTER HIEBER (*Ber.*, 1919, 52, [B], 731-741).—In a previous communication (*Zeit. anorg. Chem.*, 1919, 106) it has been shown that trivalent iron forms a complex cation with hypophosphorous acid, $[\text{Fe}_3(\text{H}_2\text{PO}_2)_6]^{+++}$. It is now established that a similar complex anion can also exist. If the basic ferric hypophosphite, $\text{Fe}_3(\text{H}_2\text{PO}_2)_6\cdot\text{OH}$, is dissolved in warm concentrated solutions of alkali hypophosphites and the solutions are allowed to evaporate, pale reddish-violet crystals separate having the composition $\text{Fe}(\text{H}_2\text{PO}_2)_3\cdot 2\text{K}(\text{Na})\text{H}_2\text{PO}_2\cdot\text{H}_2\text{O}$. The molecule of water is firmly retained. The properties of these salts lead the authors to ascribe to them the constitution $[\text{Fe}_3(\text{H}_2\text{PO}_2)_6]^{--}[\text{K}_2(\text{Na})_2]$. When the salts are dissolved in water, a basic ferric hypophosphite is precipitated,

$$3[\text{Fe}_3(\text{H}_2\text{PO}_2)_6]^{--}[\text{K}_2] = [\text{Fe}_3(\text{H}_2\text{PO}_2)_6]^{--}(\text{H}_2\text{PO}_2)_2 + \text{H}_3\text{PO}_2 + 6\text{KH}_2\text{PO}_2 + 2\text{H}_2\text{O},$$

a complex cation being thus transformed into a complex anion; the latter is only stable in solution in the presence of a large excess of alkali hypophosphite, and the composition of the basic salt varies somewhat.

Since hypophosphorous acid and ferric iron can thus combine to form both complex acid and complex base, it is to be expected that these will combine with one another to yield salts which appear to be ferric hypophosphites. Their constitution follows from their mode of formation. Thus, if concentrated ferric chloride solution

is slowly added to warm concentrated alkali hypophosphite, the ferric hypophosphite formed is immediately dissolved, yielding the complex pentahypophosphito-ion; on continued addition, however, a sudden precipitation occurs, and further precipitations can be obtained from the successive filtrates. These salts are all feebly basic or practically neutral, the composition of which varies between $\text{Fe}:\text{H}_2\text{PO}_2=1:2.71$ and $1:2.86$. Salts are thus obtained containing (i) two hexahypophosphito-cations, one pentahypophosphito-anion, and two hypophosphite radicles; (ii) a similar salt containing three hypophosphite radicles, and (iii) a salt composed of one complex anion and cation. Similarly, when a solution of ferric hypophosphite in hypophosphorous acid (50%) is evaporated over sulphuric acid, a salt is obtained containing one triferrihexahypophosphito-cation and one pentahypophosphito-anion, and either three or four molecules of hypophosphorous acid.

The ability of hypophosphorous acid to yield both complex anions and cations with ferric iron is shared only by formic and salicylic acids; the reason may possibly lie in the somewhat similar structure, $\text{H}\cdot\text{C}\begin{smallmatrix} \text{O} \\ \diagup \\ \text{OH} \end{smallmatrix}$ and $\text{H}_2\cdot\text{P}\begin{smallmatrix} \text{O} \\ \diagup \\ \text{OH} \end{smallmatrix}$, of formic and hypophosphorous acids. H. W.

The Normal Nitrides of Nickel and Cobalt. A. C. VOURNASOS (*Compt. rend.*, 1919, 168, 889—891).—*Nickel nitride*, Ni_3N_2 , is readily obtained if a mixture of anhydrous nickelous oxide and anhydrous nickel cyanide in the proportion of 1:0.74 is dropped in small quantities at a time through an arc between two carbon electrodes in an atmosphere of nitrogen, providing the temperature of the arc is near 2000° . The nitride so obtained is not magnetic. It burns in oxygen, giving nickelous oxide and nitrogen peroxide. It is decomposed when heated in chlorine, and also by nitric and hydrochloric acids. It is not decomposed by boiling water.

Cobalt nitride, Co_3N_2 , a brown powder, may be similarly prepared, and possesses similar properties. W. G.

Existence of isoTungstic Acid. P. BARBE (*Mon. Sci.*, 1919, [v], 9, i, 73—75).—Results of a critical research led the author to the opinion that isotungstic acid and ammonium isotungstate do not exist; the ammonium isotungstate described by Gerber (A., 1917, ii, 575) was actually ammonium sodium tungstate. The author has worked for some years on tungsten, and, without going as far as to deny the existence of neotungsten, states that he has never met with a specimen of the metal having a molecular weight higher than usual. [See, further, *J. Soc. Chem. Ind.*, 1919, June.] W. P. S.

Mineralogical Chemistry.

Orueteite, a New Sulphotelluride of Bismuth. S. PIÑA DE RUBÍES (*Anal. Fis. Quim.*, 1919, 17, 83—87).—This mineral, discovered in the Serranía de Ronda, in Spain, occurs on dolomite in laminar masses accompanied by scheelite, pyrites, mispickel, limonite, bismuthite, and native bismuth. The laminae show a brilliant steel-grey, metallic lustre, and are easily exfoliable. Hardness, 1·5—2. Density, 7·6. The resemblance to tetradymite is very marked. The mean of seven analyses gave: Bi 86·78%, Te 6·35%, S 6·84%. This analysis is in agreement with the formula Bi_4TeS_4 . A study of the ternary system bismuth-sulphur-tellurium shows the existence of the compounds Bi_2S_3 , Bi_2Te_3 , and $\text{Bi}_2\text{Te}_3\text{Bi}_2\text{S}_3$ (Amadori, A., 1918, ii, 366), the naturally occurring sulphotellurides, tetradymite (variety with sulphur), joseite, grüningite, orueteite, being regarded as eutectic mixtures. The author proposes the following representation of these eutectics: tetradymite (with sulphur), $\text{Bi}_2\text{Te}_3\text{Bi}_2\text{S}_3$ — Bi_2Te_3 ; joseite, $\text{Bi}_2\text{Te}_3\text{Bi}_2\text{S}_3$ — $5\text{Bi}^?$; grüningite, $\text{Bi}_2\text{Te}_3\text{Bi}_2\text{S}_3$ — $2\text{Bi}_2\text{S}_3$ — 4Bi ; orueteite, $\text{Bi}_2\text{Te}_3\text{Bi}_2\text{S}_3$ — $3\text{Bi}_2\text{S}_3$ — 14Bi .

W. S. M.

Hydrated Ferric Oxides. EUGEN POSNJAK and H. E. MERWIN (*Amer. J. Sci.*, 1919, [iv], 47, 311—348).—Analyses of a number of naturally occurring hydrated ferric oxides, from many localities, have been made, and the detailed results given in the paper. Dehydration curves and specific gravities of some of the specimens have been obtained. The experiments show that there is only one hydrate of natural ferric oxide, and this is the monohydrate. The descriptions given in the literature of a series of hydrates ranging from $\text{Fe}_2\text{O}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ to $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ are therefore erroneous. The monohydrate occurs in nature in two polymorphic forms, goethite and lepidocrocite, and in an amorphous condition, limonite. Goethite is orthorhombic, $a:b:c=0.91:1.0602$, $D\ 4.28 \pm 0.01$, $\alpha\ 2.26$, $\beta\ 2.394$, $\gamma\ 2.400$; it has a dull orange-yellow streak and a faint pleochroism. Lepidocrocite is orthorhombic, $a:b:c=0.43:1.064$, $D\ 4.09 \pm 0.04$, $\alpha\ 1.94$, $\beta\ 2.20$, $\gamma\ 2.51$; it has a dull orange streak and a very strong pleochroism. Limonite is essentially isotropic ferric oxide monohydrate with adsorbed and capillary water. The fibrous mineral turgite is variable in composition, and is probably a solid solution of goethite in hematite with enclosed and adsorbed water. No definitely crystallised synthetic hydrated ferric oxide has been prepared, and only two types of amorphous hydrated ferric oxide exist, one yellow and the other reddish-brown. The yellow substance is essentially ferric oxide monohydrate, whilst the reddish-brown substance may hold its water either in a dissolved or an absorbed condition, or both.

J. F. S.

Turite (= Turgite) and other Iron-Ores from Nova Scotia.
 L. J. SPENCER (*Min. Mag.*, 1919, 18, 339—348).—The group of ferric hydroxide minerals include the following species (hæmatite being added to complete the series):

| | | H ₂ O%. | Sp. gr. |
|--------------------|--|--------------------|---------|
| Hæmatite..... | Fe ₂ O ₃ | 0.0 | 5.2 |
| Turite | 2Fe ₂ O ₃ .H ₂ O | 5.3 | 4.3 |
| Goethite | Fe ₂ O ₃ .H ₂ O | 10.1 | 4.2 |
| Hydrogoethite .. | 3Fe ₂ O ₃ .4H ₂ O | 13.1 | 3.7 |
| Limonite | 2Fe ₂ O ₃ .3H ₂ O | 14.5 | 3.9 |
| Xanthosiderite ... | Fe ₂ O ₃ .2H ₂ O | 18.4 | — |
| Limnrite | Fe ₂ O ₃ .3H ₂ O | 25.3 | 2.8 |
| Esmeraldaite | Fe ₂ O ₃ .4H ₂ O | 31.1 | 2.6 |

Of these, goethite is the only one that occurs as distinct crystals; the remainder have sometimes been regarded as colloids of indefinite composition, and in some of the recent text-books are treated all together under limonite. Turite and limonite possess, however, a fibrous, crystalline structure with definite optical characters, and their dehydration curves are quite distinct from one another and from that of goethite. Turite (the more familiar spelling, turgite, is an incorrect German transliteration from the Russian) usually occurs as a layer on limonite, and forms hard ($H=6\frac{1}{2}$), lustrous, mamillated or botryoidal masses with a radially-fibrous and concentric-shelly structure. It is black with often a reddish tinge of colour and a brilliant sub-metallic lustre; the streak is dark cherry-red, and very thin fibres transmit a crimson colour. It decrepitates violently when heated.

The other Nova Scotian iron ores include magnetite, hæmatite, chalybite, mesitite, ankerite, and brilliant pseudomorphous crystals of hæmatite after goethite.

L. J. S.

The Occurrence of Polyhalite in the Older Zechstein Potassium Salt Deposits in Relation to Van't Hoff's Conclusions. M. ROSZA (*Zeitsch. anorg. Chem.*, 1919, 105, 167—170).

—The occurrence of primary and secondary deposits of polyhalite, Ca₂K₂Mg(SO₄)₄.2H₂O, is in general agreement with what is to be expected from van't Hoff's work. The salt is met with in almost all potassium-containing parts of the older Zechstein salt deposits, with the exception of the carnallite layers. As a primary deposit, it is found here and there in the "Steinsalz." Elsewhere, as in the kieserite transition zone of the Stassfurt carnallite layer, it is represented by its decomposition products, anhydrite, kieserite, sylvine, and carnallite, formed through the infiltration of liquors rich in magnesium chloride from the carnallite region. Where the carnallite-kieserite layers have undergone hydrothermal change, the conditions may have become favourable for the formation of polyhalite as a secondary deposit. Where hard salt formation has taken place under conditions which would preclude the formation of polyhalite, or where only a purely thermal decomposition of carnallite has occurred, no polyhalite is found. The presence of polyhalite is of great importance from the point of view of chemical genetics.

E. H. R.

The Presence of Boron in some Natural Basic Silico-aluminates. A. LACROIX and A. DE GRAMONT (*Compt. rend.*, 1919, 168, 857—861).—A spectrographic study of three basic silico-aluminates from Madagascar, saphirine, grandidierite, and kornerupine (compare A., 1912, ii, 1182), revealed the presence of boron, and this was confirmed by a further chemical analysis. The boron content of the minerals increased in the order named. The authors consider that boron replaces aluminium isomorphously in these minerals. A number of other silico-aluminates were also examined spectrographically. Boron was found in dumortierite and certain idocrases, whilst in other idocrases its presence was not detected. Similarly, it could not be detected in andalusite, sillimanite, disthene, or in the natural hydrated aluminas examined.

W. G.

Ferrierite, a New Zeolitic Mineral, from British Columbia.

R. P. D. GRAHAM (*Trans. Roy. Soc. Canada*, 1918, [iii], 12, Sect. IV, 185—190).—The mineral occurs in veins of chalcedony and calcite in decomposed basalt on the north shore of Kamloops Lake. It forms white, spherical aggregates of colourless, orthorhombic blades with a perfect pearly cleavage parallel to (100), D 2.150, H 3—3½, α 1.478, β 1.479, γ 1.482. Analysis of the transparent blades carefully freed from chalcedony gave:

| SiO ₂ | Al ₂ O ₃ | CaO | MgO | Na ₂ O | K ₂ O | H ₂ O | Total |
|------------------|--------------------------------|-----|------|-------------------|------------------|------------------|--------|
| 69.13 | 11.44 | nil | 2.92 | 3.97 | 0.36 | 13.05 | 100.87 |

corresponding with Clarke's general formula for ptilolite and mordenite, namely, $Al_2(Si_2O_5)_2R'_4 + 6H_2O$, where $R'_2 = Mg, Na_2, H_2$. Ferrierite, however, differs from all other zeolites in containing magnesium in place of calcium. The mineral commences to lose water at or below 100°; about half is lost at 205°, whilst at 275° 5.71% is still retained, and is probably in part basic.

L. J. S.

Scapolite from the Kiruna District, Swedish Lapland.

NILS SUNDIUS (*Akad. Abhandl. Upsala*, 1915, 197—224, and *Vetenskapliga och praktiska undersökningar i Lappland, anordnade av Luossavaara-Kiirunavaara Aktiebolag*; from *Jahrb. Min.*, 1918, Ref. 255—257).—The rocks of this district are rich in scapolites, which are very fresh and form fine-grained masses or large, prismatic aggregates. They have been produced by regional pneumatolytic metamorphism, the chlorine, carbon dioxide, and sulphur trioxide having been introduced by magmatic emanations, whilst the other constituents have been derived from the felspars of the pre-existing rocks. Analysis I is of scapolite from amphibolite at Vahäive, II from greenstone at Pahtosvaara, and III from scapolite-diopside-amphibolite at Kalpivaara.

| | SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | CaO | Cl | F | SO ₃ | CO ₂ | Sp. gr. |
|------|------------------|--------------------------------|--------------------------------|-------|------|------|-----------------|-----------------|-------------|
| I. | 48.52 | 27.53 | 0.25 | 13.31 | 1.24 | — | 0.55 | n.d. | 2.710—2.720 |
| II. | 54.82 | 22.49 | — | 7.37 | 3.04 | — | 0.56 | n.d. | 2.632 |
| III. | 57.31 | 22.07 | — | 6.27 | 3.49 | 0.02 | 0.25 | 0.34 | 2.610 |

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The relation between the optical constants and the composition of these materials is shown in another paper by the same author (this vol.; ii, 163).
L. J. S.

Viridine and its Relation to Andalusite. E. A. WULFING (*Sitzungsber. Heidelberg. Akad. Wiss., Math.-nat. Kl.*, 1917, *Abh.* 12; from *Jahrb. Min.*, 1918, *Ref.* 259—261).—Viridine from Darmstadt (D 3·220) was described by G. Klemm (A., 1913, ii, 423) as a green variety of andalusite containing Fe_2O_3 4·16 and Mn_2O_3 4·77%, the formula being $(\text{Al}, \text{Mn}, \text{Fe})_2\text{SiO}_5$, and a similar mineral (D 3·205) from Vestana, Sweden, was described by H. Bäckström under the name manganandalusite (A., 1897, ii, 271). These are compared optically with the ordinary type of red andalusite (D 3·154) and with greenish-yellow andalusite from Brazil (D 3·162, which has not been analysed, but is probably similar to the red andalusite). Viridine is optically positive with $\gamma=c$, whilst andalusite is optically negative with $a=c$. On account of this difference, viridine is considered to be distinct from andalusite, and consequently Al_2SiO_5 is regarded as tetramorphous, as represented by the minerals kyanite, sillimanite, andalusite, and viridine.
L. J. S.

The Pelham Asbestos Mine, Massachusetts. EARL V. SHANNON (*Amer. Min.*, 1919, 4, 37—39).—Various minerals are developed at the junction of an intrusive mass of peridotite (saxonite) in acid gneiss at this locality. The outer portion of the saxonite is changed to fibrous anthophyllite, which is here mined as asbestos. Associated with biotite is a saponaceous, silvery, bluish-green mineral composed of fine scales; on drying, it becomes opaque and pale olive-green. Analyses I and II of material slightly contaminated with biotite and actinolite prove that this is the "pelhamite" of J. P. Cooke (1875), which is classed by Dana as a vermiculite.

| | | | | | | H ₂ O | H ₂ O | |
|-----|----------------|-------------------------|-------------------------|--------------|--------------|------------------|------------------|--------|
| | SiO_2 | Al_2O_3 | Fe_2O_3 | CaO | MgO | < 105°. | > 105°. | Total. |
| I. | 40·08 | 21·65 | 3·59 | 0·58 | 20·12 | 3·79 | 7·83 | 97·64 |
| II. | 38·88 | 19·27 | 3·99 | — | 22·66 | 3·36 | 9·54 | 97·90 |

L. J. S.

The Origin of Septarian Structure. W. ALFRED RICHARDSON (*Min. Mag.*, 1919, 18, 327—337).—The origin of the system of polygonal cracks in septarian nodules is discussed in detail. The expansion and contraction theories are dismissed, and it is concluded that the cracks are due to the desiccation of a colloidal centre by chemical means. Similar structures are produced artificially when pats of clay are air-dried or immersed in a concentrated solution of calcium chloride. The following partial analyses are of Ia, the exterior portion, and Ib, the central portion, of an ironstone septarium from the Lias at Bracebridge, Lincolnshire, and II of the clay in which the nodules are embedded.

III of a limestone septarium from Nottinghamshire, *a* the exterior, *b* 1 inch from the outside, and *c* the centre.

| | SiO ₂ . | Al ₂ O ₃ . | Fe ₂ O ₃ . | CaO. |
|------------|--------------------|----------------------------------|----------------------------------|------|
| Ia. 24.7 | 18.6 | 34.3 | — | |
| Ib. 13.1 | 35.1 | 4.7 | 22.9 | |
| II. 53.1 | 31.1 | 7.3 | — | |
| IIla. 12.3 | trace | 7.2 | 36.3 | |
| IIlb. 8.0 | 2.0 | 3.9 | 45.3 | |
| IIlc. 4.5 | 4.0 | 3.5 | 46.0 | |

The nodules probably originated by the rhythmic precipitation of solutions diffusing through a colloid according to Liesegang's laws. L. J. S.

Analytical Chemistry.

A Simplification of the McLean-van Slyke Method for Estimation of Plasma Chlorides. DONALD D. VAN SLYKE and JOHN J. DONLEAVY (*J. Biol. Chem.*, 1919, **37**, 551—555).—The method previously described (A., 1915, ii, 573) has been simplified by reducing the number of filtrations necessary. The standard silver nitrate solution is made up to contain, in addition to the nitrate, 7.5 grams of picric acid per litre. This solution precipitates both protein and chlorides simultaneously. The excess of silver in the filtrate is titrated with potassium iodide.

J. C. D.

Indirect Electrolytic Estimation of Anions without Platinum Electrodes. E. LASALA (*Anal. Fis. Quim.*, 1919, **17**, 83—95).—The present preliminary investigation is concerned with the estimation of chloride, bromide, and iodide. The halogen is precipitated as silver haloid by means of a 5% solution of silver nitrate. The precipitate is filtered through glass wool and dissolved in 20% solution of potassium cyanide to which a little sodium hydroxide is added. The solution is electrolysed with a nickel-plated copper cathode and a rotating iron anode. Towards the end of the electrolysis, the electrolyte is heated nearly to boiling. The results are most satisfactory. The cathode is prepared by electrolysis of an ammoniacal solution of nickel sulphate.

W. S. M.

Iodometric Studies. The Starch-Iodine Reaction. I. M. КОЛТНОВ (*Pharm. Weekblad*, 1919, **56**, 391—404).—A systematic investigation of the sensitiveness of the starch-iodine reaction under varying conditions. The sensitiveness is increased by the presence of salts, especially potassium iodide, and acids (A., 1895, i, 79). Increased temperatures and presence of organic substances

such as alcohols, albumin, etc., diminish the sensitiveness. The magnitude of the correction to be applied in the titration of dilute iodine solutions with dilute thiosulphate solutions, and vice versa, was determined. The correction is a minimum in hydrochloric acid solution to which a little potassium iodide has been added.

W. S. M.

The Iodometric Estimation of Bromate (and Iodate). I. M. KOLTHOFF (*Pharm. Weekblad*, 1919, 56, 426—438).—In the titration with thiosulphate solution of bromate solutions to which potassium iodide has been added, the concentrations of bromate and iodide are factors of little importance. It is essential, however, that sufficient acid be present in the mixture. The minimum concentration required in the solution is 0.5*N* for hydrochloric acid and about 1.0*N* for sulphuric acid if titration is carried out immediately after the addition of the iodide. If too little acid is present, oxidation of the thiosulphate directly to sulphate takes place: $8\text{HBrO}_3 + 5\text{H}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O} = 10\text{H}_2\text{SO}_4 + 4\text{Br}_2$ or $4\text{HBrO}_3 + 3\text{H}_2\text{S}_2\text{O}_3 + 3\text{H}_2\text{O} = 6\text{H}_2\text{SO}_4 + 4\text{HBr}$. In either case, too little of the thiosulphate solution is required. The error may be avoided by allowing the mixture to remain some time before titration, or by the addition of a catalyst. The best catalyst is ammonium molybdate in both strong and weakly acid solutions. The catalytic effect of ferrous sulphate and potassium dichromate is negligible in strongly acid solutions, but is more marked in weakly acid solutions. Light has a positive catalytic effect. Salts such as sodium chloride and sodium sulphate retard the reaction.

The reaction between iodate and iodide is much more rapid than that between bromate and iodide, and therefore the iodometric estimation of iodates is not attended by the difficulties arising in the latter case.

W. S. M.

A Simple Form of Apparatus for Estimating the Oxygen Content of Air from the Upper Atmosphere. FRANCIS WILLIAM ASTON (T., 1919, 115, 472—475).

Sodium Pyrogalloxide Solution as an Absorbent for Oxygen. G. W. JONES and M. H. MEIGHAN (*J. Ind. Eng. Chem.*, 1919, 11, 311—316).—The rate of oxygen absorption in sodium pyrogalloxide solutions increases with the dilution of the sodium hydroxide; for any given concentration of sodium hydroxide, the rate of absorption is proportional to the concentration of the pyrogallol. Carbon monoxide is evolved from the solution if the sodium hydroxide solution used has a specific gravity of less than 1.30; all sodium pyrogalloxide solutions evolve carbon monoxide if the sample under examination contains more than 95% of oxygen. A reagent which evolves the minimum quantity of carbon monoxide and has a fairly high rate of absorption is made by dissolving sodium hydroxide in its own weight of water and adding five parts

of this solution to two parts of a solution containing 1 gram of pyrogallol in 3 c.c. of water.

W. P. S.

The Relation between the Oxygen Concentration and Rate of Reduction of Methylene-blue by Milk. E. NEWTON HARVEY (*J. Gen. Physiol.*, 1919, 1, 415—419).—The rate of reduction and decolorisation of methylene-blue by milk in the presence of an aldehyde is proportional to the oxygen concentration. It is suggested that this fact might be made the basis of a method for determining the oxygen content of gaseous mixtures. Carbon dioxide present in concentrations up to 5% does not affect the reducing action of the milk.

J. C. D.

Method for the Identification of Sulphur-Oxygen Compounds. A. SANDER (*Chem. Zeit.*, 1919, 43, 173. Compare A., 1915, ii, 161).—Sulphates, sulphites, hydrogen sulphites, thio-sulphates, sulphides, and polythionates may be identified by their different behaviour towards mercuric chloride, this reagent also serving, to a certain extent, for the identification of the compounds in the presence of each other. The following reactions result when the compounds are treated with an excess of mercuric chloride solution. *Sodium Sulphate*.—Mercuric sulphate and sodium chloride are formed, and the solution remains neutral in reaction. *Sodium Sulphite*.—The solution remains clear and is alkaline towards methyl-orange before and after the addition of mercuric chloride; when the mixture is boiled, it becomes acid and calomel is precipitated. *Sodium Hydrogen Sulphite*.—No precipitate; boiling produces a precipitate and the mixture remains acid. *Sodium Sulphide*.—A black precipitate, which rapidly becomes white owing to the formation of a sulphochloride; the mixture has a neutral reaction before and after boiling. *Sodium Thiosulphate*.—As in the case of a sulphide, a white precipitate forms, but the mixture becomes strongly acid; it remains acid when boiled. *Sodium Polythionate*.—Behaves like sodium thio-sulphate towards mercuric chloride, but may be distinguished from the latter in that it does not decolorise iodine solution and does not give a precipitate of sulphur when acidified. Sulphite and polythionate cannot exist together in the same solution.

W. P. S.

Volumetric Estimation of Sulphurous Acid. THOS. J. I. CRAIG (*J. Soc. Chem. Ind.*, 1919, 38, 96r).—The sulphurous acid solution is added to a known excess of hydrogen peroxide solution acidified with dilute sulphuric acid, and the excess of hydrogen peroxide is then titrated with standardised potassium permanganate solution. The reaction proceeds according to the equations $\text{SO}_2 + \text{H}_2\text{O}_2 = \text{H}_2\text{SO}_4$, and $5\text{H}_2\text{O}_2 + 2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 = \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 8\text{H}_2\text{O} + 5\text{O}_2$. The method may also be applied to solutions containing sulphites or hydrogen sulphites.

W. P. S.

Estimation of Total Nitrogen, including Nitric Nitrogen [in Soil Extracts]. B. S. DAVISSON and J. T. PARSONS (*J. Ind. Eng. Chem.*, 1919, **11**, 306—311).—The method recommended consists in boiling the soil extract solution with a quantity of sodium hydroxide sufficient to make the alkalinity approximately $N/10$, reduction of the nitric nitrogen being effected by the addition of Devada's alloy. The boiling flask is connected with an absorption tube containing an excess of sulphuric acid (4:1). The contents of the absorption tube are then washed into the flask, the mixture is evaporated until charring commences, potassium sulphate is added, and the digestion continued. The ammonia formed is distilled after the addition of sodium hydroxide and sodium sulphide. [See, further, *J. Soc. Chem. Ind.*, 1919, 332A.]
W. P. S.

Estimation of Nitrous Acid and Nitrites. J. S. LAIRD and T. C. SIMPSON (*J. Amer. Chem. Soc.*, 1919, **41**, 524—531).—The volumetric methods for the estimation of nitrous acid and nitrites, as described in the literature, have been experimentally examined and shown to be unsatisfactory. The authors have devised a method for estimating nitrites which consists in the oxidation of the nitrite in acid solution with excess of potassium permanganate, reduction of the excess of permanganate by an excess of ferrous sulphate, sodium oxalate, or hydrogen peroxide, and titration of the excess of the reducing agent by permanganate. In the actual estimation, the nitrite is run slowly into the excess of permanganate, acidified with 1:4-sulphuric acid, and constantly shaken. The titration is not interfered with by moderate amounts of chloride or small amounts of bromide. Silver nitrite is not a satisfactory material for use as a standard in nitrite estimations. A satisfactory standard solution may be made by titrating sodium nitrite solution with potassium permanganate according to the method described above, or sodium nitrite solution may be standardised gravimetrically by the reduction of silver bromate to silver bromide according to Busvold's method (*A.*, 1914, ii, 144).
J. F. S.

Gravimetric Estimation of Phosphoric Acid as Magnesium Pyrophosphate. Z. KARAOGLANOW (*Zeitsch. anal. Chem.*, 1918, **57**, 497—541).—An investigation of the different methods employed for the precipitation of phosphoric acid as ammonium magnesium phosphate previous to the conversion of the precipitate into magnesium pyrophosphate. To a slight extent, the precipitation depends on temperature, rate of precipitation, and presence of varying quantities of magnesium chloride, ammonium chloride, etc.: the differences in the final results are usually very small. The lack of a more trustworthy method for the estimation of phosphoric acid and the difficulty of obtaining a substance of known phosphorus content render it impossible to say which method of precipitation gives the true quantity of phosphoric acid present.
W. P. S.

Gravimetric Analysis. X. XII. Estimation of Phosphoric Acid. L. W. WINKLER (*Zeitsch. angew. Chem.*, 1919, **32**, 98—101).—Precipitation of phosphoric acid as ammonium magnesium phosphate and weighing it as such or after ignition to magnesium pyrophosphate, yields trustworthy results. The presence of large quantities of potassium and sodium chlorides does not influence the results when the precipitate is weighed in the form of ammonium magnesium phosphate, but when the precipitate is converted into pyrophosphate, the result is too high if potassium chloride was present in the solution. [See, further, *J. Soc. Chem. Ind.*, 1919, 391A.]

W. P. S.

Estimation of Arsenic in Volatile Cacodyl Compounds. L. C. MAILLARD (*Bull. Soc. chim.*, 1919, [iv], **25**, 192—200).—The method is based on the oxidation of the cacodyl compound to cacodylic acid, and subsequently to arsenic acid. The arsenic is then separated in the usual manner by precipitation as magnesium ammonium arsenate, and weighed as pyroarsenate. For the first stage of the oxidation, a suitable weight of the cacodyl compound, in a sealed bulb if liquid or in a narrow tube if solid, is introduced into a flask containing 3 grams of ammonium persulphate, 30 c.c. of water, and 10 c.c. of sulphuric acid. The flask is quickly closed with a ground-in stopper and thoroughly shaken until the air in the flask, at first cloudy, is quite clear. Ten c.c. of fuming nitric acid are now added, and the estimation proceeded with in the usual way, the arsenic being first precipitated as its sulphide if necessary and then redissolved before finally precipitating it as the double arsenate. The method was applied to cacodyl chloride, and found to be simple and accurate.

W. G.

Gravimetric Analysis. XI. XIII. Estimation of Arsenic Acid. L. W. WINKLER (*Zeitsch. angew. Chem.*, 1919, **32**, 122—124).—Two methods are described for the estimation of arsenic acid. In the first, the arsenic acid is treated with potassium thiocyanate, then with hydrogen sulphide, and the precipitate, consisting of arsenic trisulphide and sulphur, is collected, dried at 100°, and weighed: $\text{As}_2\text{O}_5 + 2\text{KCNS} = 2\text{KOCN} + \text{As}_2\text{O}_3 + \text{S}_2$; $\text{As}_2\text{O}_3 + 3\text{H}_2\text{S} = \text{As}_2\text{S}_3 + 3\text{H}_2\text{O}$. The second method consists in the precipitation of the arsenic acid as ammonium magnesium arsenate; details of the procedure are given in full. Arsenious acid solutions may be oxidised by hydrogen peroxide in the presence of ammonia, and the arsenic then precipitated as ammonium magnesium arsenate. [See, further, *J. Soc. Chem. Ind.*, 1919, June.]

W. P. S.

Selection of an Indicator for the Acidimetric Estimation of Boric Acid. JOHANNES PRESCHER (*Zeitsch. Nahr. Genussm.*, 1918, **36**, 283—286).—Phenolphthalein is considered to be the most suitable indicator for the purpose.

W. P. S.

Electrical Precipitator for Analysing Smokes. RICHARD C. TOLMAN, L. H. REYERSON, A. P. BROOKS, and H. D. SMYTH (*J. Amer. Chem. Soc.*, 1919, **41**, 587—589).—A modified form of the Cottrell precipitator is described which has been used for removing the solid particles from smokes. The apparatus consists of a glass tube 1.6 cm. in diameter and 25 cm. long, a thin aluminium foil cylinder 0.025 mm. thick is placed in the glass tube and constitutes the anode, and a cathode consisting of a No. 25 platinum wire threaded with a jeweller's die passes centrally down the aluminium cylinder. Entrance and exit tubes for the smoke are attached at the ends. A high-voltage circuit (15,000 volts) is attached to the electrodes, and a corona discharge produced; sparking must be avoided. The smoke is then admitted at the rate of 5 litres per minute, when the negatively charged particles are deposited on the aluminium foil. The weight of particles is determined by weighing the anode before and after the precipitation. J. F. S.

Characterisation and Estimation of Carbonyl Chloride. ANDRÉ KLING and RENÉ SCHMUTZ (*Compt. rend.*, 1919, **168**, 773—775).—Carbonyl chloride readily reacts with an excess of aniline in saturated aqueous solution to give diphenylcarbamide and aniline hydrochloride. Thus a trace of carbonyl chloride in air may readily be detected by bubbling 5 litres of the air at the rate of 1 litre in five minutes through the aqueous solution of aniline, and characterising the precipitate microscopically and by its m. p. as diphenylcarbamide, which is practically insoluble in water. By this means, carbonyl chloride may be detected in the air at a dilution of 1 in 100,000. For the estimation of carbonyl chloride in solution in organic solvents, a quantity of the solution containing 0.2—0.35 gram of carbonyl chloride is added to 150 c.c. of the aqueous aniline solution (containing 26 grams of aniline per litre), and after two hours the mixture is heated on a water-bath for one hour to drive off the organic solvent. The liquid is allowed to cool, and the next day the precipitate of diphenylcarbamide is collected on a Gooch crucible, dried at 70°, and weighed. W. G.

Estimation of Traces of Carbonyl Chloride in Air. ANDRÉ KLING and RENÉ SCHMUTZ (*Compt. rend.*, 1919, **168**, 891—893).—Using the method previously described (preceding abstract), the carbonyl chloride may be estimated gravimetrically if the weight of diphenylcarbamide exceeds 10 mg. by dissolving the precipitate off the filter with alcohol and evaporating the alcoholic solution in a weighed platinum crucible at a temperature not exceeding 60°, after which the residue is dried at this temperature for two hours. Alternatively, a colorimetric method may be employed by digesting the precipitate and filter paper with sulphuric acid and mercuric sulphate, and proceeding as in the ordinary Kjeldahl process, the ammonia passing over being collected in *N*/250-hydrochloric acid, and finally estimated by means of Nessler's reagent. W. G.

Analyses of Mixtures of Vapours containing Carbon Monoxide, Carbon Dioxide, Carbonyl Sulphide and Carbon Disulphide and similar Mixtures of Gases. ALFRED STOCK and PAUL SEELIG (*Ber.*, 1919, 52, [B], 672—680. Compare Stock and Kuss, A., 1917, ii, 205).—The processes described depend on the difference in the rates with which the various gases or vapours are absorbed by alkali.

Carbon dioxide is immediately absorbed by alkali hydroxides of widely differing concentrations. Carbonyl sulphide is absorbed by the hydroxides of rubidium, potassium, sodium, and lithium in order of decreasing rapidity; with sodium hydroxide, the rate of absorption varies with the concentration, being at a minimum with a 30% solution; the gas is completely absorbed in about an hour. The complete absorption of carbon disulphide vapour by aqueous alkali hydroxide requires several days, whilst carbon monoxide is not absorbed.

An alternative method of estimating carbon disulphide in gaseous mixtures, which can be rapidly and accurately performed, consists in saturating a measured volume of the gas with carbon disulphide and measuring the increase in volume.

Two methods are described for the analysis of the mixture. (1) A measured volume of the gas is shaken with sodium hydroxide solution (30%, 1 c.c.), and the volume read off each minute during several minutes (CO_2). Water (4 c.c.) is now added, and the gas volume is determined every ten minutes for about an hour (COS). Potassium hydroxide (30%, 1 c.c.) is now added, and the volume recorded after one, two, three, etc., days (CS_2). The residue is carbon monoxide, which must be completely absorbed by cuprous chloride solution. (2) Carbon dioxide is estimated in one portion as usual. A second portion is intermittently shaken with sodium hydroxide (2—3 c.c., 50%); after fifteen to thirty minutes, shaking is made continuous, and the volume read off each minute until it is constant ($\text{CO}_2 + \text{COS}$). A third portion is shaken occasionally with potassium hydroxide (5%, 2—3 c.c.), and the volume determined daily until constant ($\text{CO}_2 + \text{COS} + \text{CS}_2$), the residual carbon monoxide being tested for purity by means of ammoniacal cuprous chloride solution. Alternatively, the residue obtained after absorption of CO_2 and COS may be saturated with carbon disulphide and the increase in volume determined.

The paper also contains a vapour tension-temperature table for aqueous sodium hydroxide solutions of differing concentration and for carbon disulphide, for which the data given in the literature are somewhat discordant.

H. W.

Estimation of Alkali in Permanganate Liquors. THOS. J. I. CRAIG (*J. Soc. Chem. Ind.*, 1919, 38, 96—97r).—The method depends on the reaction between permanganate and hydrogen peroxide. $5\text{H}_2\text{O}_2 + 2\text{KMnO}_4 = 2\text{KOH} + 2\text{MnO}_2 + 4\text{H}_2\text{O} + 4\text{O}_2$. After filtration, the alkalinity is estimated by titration; the alkalinity due to the permanganate is deducted from the result, and the

remainder represents the quantity of free alkali (hydroxide or carbonate) in the solution. With manganates, the reaction proceeds according to the equation $\text{H}_2\text{O}_3 + \text{Na}_2\text{MnO}_4 = 2\text{NaOH} + \text{MnO}_2 + \text{O}_2$. In analysing mixtures containing both permanganate and manganate, the proportions of these compounds may be found by treating a portion of the solution with carbon dioxide or sodium hydrogen carbonate to convert the manganate into permanganate, $3\text{Na}_2\text{MnO}_4 + 2\text{CO}_2 = 2\text{NaMnO}_4 + 2\text{Na}_2\text{CO}_3 + \text{MnO}_2$; the precipitated manganese dioxide (which contains manganese equivalent to one-third of the manganate) is collected, and its quantity estimated by titration with ferrous sulphate and permanganate solutions.

W. P. S.

3 **Conditions affecting the Precise Estimation of Zinc as the Sulphide.** HAROLD A. FALES and GERTRUDE M. WARE (*J. Amer. Chem. Soc.*, 1919, **41**, 487—499).—The conditions affecting the quantitative estimation of zinc as sulphide have been investigated. It is shown that a hydron concentration lying between 10^{-2} and $10^{-3}N$ is most favourable for the quantitative precipitation of zinc sulphide in a form suitable for rapid filtration and washing. The concentration of the hydron may be kept within this range by the use of ammonium citrate or a mixture of ammonium sulphate, ammonium formate, and formic acid. The precipitation of granular zinc sulphide is favoured, not only by a concentration of hydron within the above-mentioned limits, but also by a high concentration of an ammonium salt of a strong acid, by a concentration of 1 gram of zinc per litre of solution, and by a temperature of $95-100^\circ$. It is desirable that the hydrogen sulphide should be passed in under pressure for the purpose of obtaining rapid saturation and avoiding loss of formic acid by evaporation. The authors recommend the following method of procedure. The zinc solution, which has been freed from cadmium, copper, and other elements likely to be precipitated, is evaporated to 125 c.c. and treated with ammonium hydroxide until the precipitate at first formed fails to redissolve, 25 c.c. of a citrate solution (200 grams of citric acid per litre of water neutralised by $15N$ -ammonia) are added, and the whole solution is made neutral to methyl-orange with ammonia. Then 25 c.c. of formic acid mixture (30 c.c. of $15N$ -ammonium hydroxide, 200 c.c. of $13.6N$ -formic acid and 250 grams of ammonium sulphate in 1000 c.c. of water) are added, and the whole is made up to 200 c.c. The solution is heated to 60° and connected with a hydrogen sulphide generator, so that air is slowly expelled from the flask as the heating is continued. At $90-100^\circ$, the flask exit is closed, and the solution as it cools saturated with hydrogen sulphide under increasing pressure. The flask should be shaken frequently to ensure saturation, which is usually complete when the precipitate settles rapidly. The precipitate is filtered and washed with a cold $0.1N$ -solution of formic acid saturated with hydrogen sulphide. The precipitate is transferred to a weighed porcelain crucible and

the filter paper charred. The completion of the ignition of the filter paper should be carried out in an oxidising atmosphere, and the reaction should proceed so that the sulphide is converted into sulphate and not into oxide. After cooling, the precipitate is moistened with concentrated sulphuric acid and heated in an air bath until the excess of acid is expelled, and then heated over a flame to remove any charred material. The mass is again moistened with sulphuric acid and heated in the air to expel the excess of acid, allowed to cool in a desiccator, and weighed. The last process is repeated until a constant weight is obtained. A modification of the above process is described which enables zinc to be quantitatively separated from iron, manganese, nickel, and cobalt. The processes described are accurate to one part per thousand.

J. F. S.

Separation of Lead in Metallic Calcium and "Lurgie" Metal. J. KÖNIG (*Chem. Zeit.*, 1919, **43**, 135).—The metal is dissolved in nitric acid, the solution neutralised with ammonia, treated with an excess of bromine-water, then rendered ammoniacal, cooled, and filtered. The lead is thus removed completely, and the calcium may be estimated in the filtrate by precipitation as oxalate. In the case of "lurgie" metal, barium must be separated as sulphate before the calcium is precipitated. [See, further, *J. Soc. Chem. Ind.*, 1919, 370a.]

W. P. S.

The Electrolytic Estimation of Mercury without Platinum Electrodes. J. GUZMÁN and P. POCH (*Anal. Fis. Quím.*, 1918, **16**, 742—755).—*Estimation in Nitric Acid Solution.*—A copper cathode and a graphite anode are used. The cathode is plated with a brilliant deposit of silver from cyanide solution, and is then washed successively in boiling water, alcohol, and ether. The mercury solution must be only slightly acid, and in order to preserve the anode, the voltage must not exceed three volts. The electrolysis is carried out in the cold. By this method, results with a maximum error of 0.3% are obtained. A similar procedure with mercuric chloride solution gives results which are less satisfactory. Excellent results are obtained with the silvered cathode and a fine platinum spiral as anode, and also with a copper cathode plated with copper by electrolysis in copper sulphate solution acidified with nitric acid. The presence of the chlorine ion is detrimental. The copper cathode may be used seven or eight times, but after every analysis the mercury must be removed by heating, and the silver with cyanide solution.

Estimation in Ammoniacal Solution.—The anode is of iron which has been heated to redness and allowed to cool in the air. A voltage of 2.4 volts is employed. The copper cathode is first nickel-plated and then covered with a deposit of silver. It is found that, after the first analysis, the employment of the same cathode, even after re-plating, gives results which are no longer quantitative, as the mercury forms a grey powder on washing with

alcohol. The same difficulty is found with cathodes on which had been deposited protective layers of gold, tin, or bismuth. The only cathode which can be used repeatedly is of copper with a deposit of mercury from electrolysis in mercuric nitrate solution. The deposit must be polished by brushing after each determination. The electrolysis is carried out in mercuric nitrate solution to which has been added ammonium nitrate and concentrated ammonia solution. The method is accurate within 0.3%.

Estimation in Alkaline Cyanide Solution.—In this case, the cathode is of copper with a brilliant deposit of silver, and the anode of iron. Sodium hydroxide solution in excess is added to a mercuric nitrate solution, and then just sufficient potassium cyanide to dissolve the precipitate formed. This electrolyte is maintained at 50° during the electrolysis. Voltage, 2.5 volts. The maximum error observed is less than 0.2%. Satisfactory results are obtained by this method in presence of the chlorine ion if the iron anode is replaced by graphite. The method is applicable to the analysis of commercial products containing mercury.

Estimation in Alkaline Sulphide Solution.—The electrolyte is prepared by dissolving precipitated mercuric sulphide in sodium sulphide solution and adding sodium hydroxide solution. With a cathode of amalgamated copper and an anode of iron, the results are moderately satisfactory, but the cathode cannot be used for a repetition of the analysis even after brushing. The addition of potassium cyanide and carbamide to the electrolyte does not lead to any marked improvement in the results. W. S. M.

Gravimetric and Volumetric Estimation of Mercury Precipitated as Mercury Zinc Thiocyanate. GEORGE S. JAMIESON (*J. Ind. Eng. Chem.*, 1919, 11, 296—297).—A solution of a mercuric salt or compound (containing about 0.14 gram of mercury) is treated with 25 c.c. of a solution containing 39 grams of ammonium thiocyanate and 29 grams of zinc sulphate per litre. The precipitate of mercury zinc thiocyanate formed is collected, washed with a solution prepared by diluting 5 c.c. of the thiocyanate reagent with 450 c.c. of water, dried at 105°, and weighed. The weight of the precipitate is multiplied by 0.40258 to obtain the quantity of mercury present. The volumetric method consists in treating the moist precipitate with 35 c.c. of concentrated hydrochloric acid, 10 c.c. of water, and 7 c.c. of chloroform, and titrating the mixture with standardised potassium iodate solution. [See further, *J. Soc. Chem. Ind.*, 1919, 341a.] W. P. S.

Estimation of Uranium in Alloy Steels and Ferro-uranium. G. L. KELLEY, F. B. MEYERS, and C. B. ILLINGWORTH (*J. Ind. Eng. Chem.*, 1919, 11, 316—317).—The sample is dissolved in hydrochloric acid, nitric acid is added, and silica and tungstic acid are separated; the greater part of the ferric chloride is then removed by extraction with ether, the solution is boiled with the addition of an excess of sodium carbonate, and filtered.

The filtrate, containing the uranium together with molybdenum and vanadium, is acidified with sulphuric acid, boiled, rendered ammoniacal, and again boiled. Uranium and some vanadium are precipitated; the precipitate is heated with ammonium carbonate solution, the mixture filtered to remove traces of manganese, iron, etc., and the filtrate acidified with sulphuric acid, boiled, and the uranium and vanadium reprecipitated by ammonia. The precipitate is collected, ignited, and weighed. The small quantity of vanadium it contains is estimated by titration with permanganate solution after solution in hydrochloric acid, or by oxidation with ammonium persulphate and silver nitrate, followed by electrometric titration. [See, further, *J. Soc. Chem. Ind.*, 1919, June.]

W. P. S.

Analysis of Natural Gas and the Calculation and Application of Results. R. P. ANDERSON (*J. Ind. Eng. Chem.*, 1919, 11, 299—306).—An indicator is described for showing complete combustion of the sample when the natural gas is passed slowly into oxygen in which an electrically heated platinum spiral is glowing; this indicator consists of a narrow glass tube connected by means of a T-piece with the rubber tubing connecting the combustion pipette with the levelling bulb; when the gas has been passed into the pipette, the tap on the levelling bulb is closed, and the contractions of the gases in the pipette are shown by the fall of the level of mercury in the narrow tube. When this fall ceases, combustion is complete. The combustion pipettes should be made of Pyrex glass. Calculation of results of combustions of natural gas according to theoretical equations is discussed, and tables of correction factors are given.

W. P. S.

Detection of Methyl Alcohol. E. SALKOWSKI (*Zeitsch. Nahr. Genussm.*, 1918, 36, 262—270).—Tests which depend on the oxidation of the methyl alcohol by potassium permanganate and on the detection of the formaldehyde produced are fairly trustworthy when applied to mixtures of methyl alcohol and pure ethyl alcohol, since the latter does not yield formaldehyde. Higher alcohols (propyl, isobutyl, and isoamyl), however, yield distinct quantities of formaldehyde when oxidised by permanganate; the colorations obtained are less intense than those yielded by methyl alcohol, and the tests may be used, with due caution, for the detection of methyl alcohol in ethyl alcohol. Only small quantities of higher alcohols are likely to be present in commercial alcohol, whilst alcohol deliberately adulterated with methyl alcohol usually contains not less than 10% of the latter. [See, further, *J. Soc. Chem. Ind.*, 1919, 382A.]

W. P. S.

[A Case of Poisoning by Methyl Alcohol and] a Simple Method of Distinguishing between Methyl Alcohol and Absolute Ethyl Alcohol or Spirit. TH. SABALITSCHKA (*Ber. Dent. pharm. Ges.*, 1919, 29, 214—219).—In connexion with a

case of poisoning due to the substitution of methyl alcohol for ethyl alcohol, the author has elaborated the following method for distinguishing between these substances. The specimen (2 c.c.) is frequently shaken during ten minutes with powdered crystalline copper sulphate (0.1 gram), and the solution is filtered. The filtrate is treated with water (5 c.c.) and ammonia solution (10%, 3 c.c.); with methyl alcohol, a deep blue to blue coloration is developed, whilst with ethyl alcohol the solution is only coloured a faint, pale blue. The method may also be used to obtain an approximate estimation of methyl alcohol in mixtures of the latter with absolute alcohol, providing the content is not less than 20%; if this is the case, the specimen must be distilled and the test performed on the first portion of the distillate. In the presence of water, even in small quantities, the process is useless, since the solutions of hydrated salts in alcohol are unstable, and the presence of water promotes separation of the salt.

Copper sulphate may also be replaced by crystalline ferrous sulphate. In this case, separation of the salt occurs with greater readiness, and the sample should only be shaken with the sulphate for five minutes. The presence of iron in the filtrate is detected by addition of water (5 c.c.) and 2.5% potassium ferricyanide solution (2 c.c.), the colorations obtained ranging from dark blue with methyl alcohol to pale green with ethyl alcohol. H. W.

Estimation of Ethyl Ether in Blood. J. W. LE HEUX (*Zeitsch. physiol. Chem.*, 1919, **104**, 137—140).—The method of Nicloux ("Les Anesthésiques Généraux," Paris, 1908) has been modified so as to increase the accuracy. Ten c.c. of blood are mixed with 65 c.c. of a saturated solution of picric acid, and the ethyl ether removed by distillation. The ether in the distillate is quantitatively oxidised to acetic acid by chromic acid, and the excess of chromic acid determined by the iodometric method. J. C. D.

A New Method for Estimating small amounts of Dichloroethyl Sulphide (Mustard Gas). E. F. HOPKINS (*J. Pharm. Expt. Ther.*, 1919, **12**, 393—403).—See this vol. i, 250.

Estimation of the Different Constituents of a Mixture containing Eugenol, Triacetin, and Benzyl Alcohol. H. PERFEROT (*Ann. Chim. anal.*, 1919, [ii], **1**, 112—114).—The quantity of triacetin is calculated from the saponification number of the mixture, whilst the iodine number is a measure of the amount of eugenol present. A portion of the mixture is also acetylated in the usual way, and the saponification number of the acetylated product is estimated; after deducting the amount due to triacetin and acetylated eugenol, the remainder is a measure of the acetylated benzyl alcohol. [See, further, *J. Soc. Chem. Ind.*, 1919, 387A.] W. P. S.

Estimation of Thymol. E. MOLES and M. MARQUINA (*Anal. Fis. Quím.*, 1919, **17**, 59—83).—See this vol. i, 270.

Estimation of small Quantities of Acetone, Alcohol, and Benzene in Air. S. ELLIOTT and J. DALTON (*Analyst*, 1919, **44**, 132—136).—The air under examination is aspirated through four absorption cylinders fitted with Folin tubes (*J. Biol. Chem.*, 1912, **11**, 493) connected by means of long rubber tubing with siphon bottles. For the estimation of acetone, one of the absorption vessels is charged with standard iodine and sodium hydroxide solutions, and the excess of iodine subsequently titrated, as in Messinger's method (*A.*, 1889, 313). No appreciable amount of iodoform is formed by the alcohol vapour in the air if the temperature is kept low. Alcohol is estimated by Szeberényi's method (*A.*, 1915, ii, 292) of oxidising it to acetic acid by means of a mixture of potassium dichromate and dilute sulphuric acid, whilst Pfeiffer's method (*A.*, 1904, ii, 786), in which the benzene is nitrated by means of a mixture of nitric and sulphuric acids, gives trustworthy results. In this case, the fourth absorption vessel is charged with sodium hydroxide solution and interposed between the acid absorption vessel and the siphons to protect the tubing. The minimum and maximum amounts of these substances per million c.c. found in the air of factories were: acetone, 0.02 to 1.86 grams, whilst the mean amount found was 0.31 gram; alcohol, 0.02 to 3.00, with a mean of 0.65 gram; benzene, 0.01 to 0.90, with a mean of 0.26 gram. [See also *J. Soc. Chem. Ind.*, 1919, 342A.]
C. A. M.

Application of the Grimbart-Leclère Reaction of apo-Morphine to Alkaloids and Adrenaline. G. DENIGES (*J. Pharm. Bordeaux*, 1918, **56**, 185; from *J. Pharm. Chim.*, 1919, [vii], 19, 49).—The reaction described by Grimbart and Leclère (*A.*, 1915, ii, 192) is also given by morphine under the following conditions. A few mg. of the alkaloid are heated with 2 drops of sulphuric acid until a slight brown coloration appears; the mixture is then diluted with 5 c.c. of saturated sodium acetate solution, 2 drops of 4% mercuric chloride solution are added, and the mixture is boiled. A green coloration is obtained. Catechol, when boiled with sodium acetate and mercuric chloride, yields a reddish-violet substance, which is soluble in ether, chloroform, and amyl alcohol. Adrenaline, treated similarly, but not heated above 50°, gives a red coloration; the reaction may be obtained with as little as 0.01 mg. of adrenaline.
W. P. S.

Estimation of the Non-Protein Nitrogenous Constituents of Milk. W. DENIS and A. S. MINOT (*J. Biol. Chem.*, 1919, **37**, 353—366).—For the estimation of total non-protein nitrogen in cows' milk, the protein and fat are removed by heating in the presence of copper sulphate. The filtrate is treated with formaldehyde, which prevents the precipitation of amino-acids as insoluble copper compounds during the subsequent removal of the lactose with cupric hydroxide. For the latter process, calcium hydroxide is preferred to sodium hydroxide, as any excess of calcium may be removed as oxalate. The total nitrogen is

estimated by conversion into ammonia with subsequent Nesslerisation (Folin and Denis, A., 1916, ii, 573). Slight modifications of this method are described for the analysis of human milk. Urea in milk may be determined by the urease method (Marshall, A., 1913, ii, 640). Ten c.c. of human or 5 c.c. of cow's milk are treated with 2 c.c. of an extract of Jack bean for thirty minutes. The ammonia produced is carried over into standard acid by a stream of air and estimated by Nesslerisation.

In the estimation of creatine and creatinine, protein may be removed by metaphosphoric acid. The presence of lactose, however, intensifies the colour reaction with picric acid, and if this method is used, equivalent amounts of the sugar should be added to the standard solution. It is perhaps better to remove protein, fat, and lactose by copper sulphate and calcium hydroxide, and to apply the colour reaction to the clear, sugar-free filtrate. Amino-nitrogen is determined by the nitrous acid decomposition method of Van Slyke (A., 1912, ii, 1008). Protein must first be removed by precipitation with acetic acid and copper acetate. For the determination of uric acid, advantage is taken of the method described by Morris (A., 1916, ii, 456). The milk is treated with acetic acid and zinc acetate solution, and heated on the water-bath for fifteen to twenty minutes. After cooling and making up to a known volume, it is filtered, and an aliquot part of the filtrate treated with zinc acetate and sodium carbonate solution. The resulting precipitate is separated by centrifugation, washed, treated with acetic acid, and the zinc removed by hydrogen sulphide. Uric acid in the concentrated filtrate is estimated by the colour reaction with Folin and Denis's reagent (A., 1912, ii, 1011). Estimations of these non-protein nitrogenous constituents in cow's milk and human milk are given.

J. C. D.

A Multiple Pipette Holder for the Distribution of Serum for the Complement-fixation Test. FRANÇOIS. H. REYNOLDS (*J. Agric. Res.*, 1918, 15, 615—618).—The pipette holder consists of a brass tube 35 cm. long and 0.94 cm. external diameter, the two ends being closed by screws or caps, and having twelve side-tubes set in one plane perpendicular to it at equal intervals along it. Another tube, to serve as a mouthpiece, is fixed on the opposite side to these tubes. The twelve side-tubes, each being 0.6 cm. in internal diameter, are lined with rubber tubing, of which the free end is folded back over the mouth of each tube, and into these are inserted the graduated pipettes. In this way, twelve lots of serum may be withdrawn at once.

W. G.

